

DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND SPECIATION
PROFILES FOR OIL AND GAS-FIRED COMBUSTION SYSTEMS

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ABSTRACT

This report provides results from the first year of this three-year project to develop dilution measurement technology for characterizing PM_{2.5} (particles with aerodynamic diameter smaller than 2.5 micrometers) and precursor emissions from stationary combustion sources used in oil, gas and power generation operations. Detailed emission rate and chemical speciation test results for a refinery gas-fired process heater and plans for cogeneration gas turbine tests and pilot-scale tests are presented. Tests were performed using a research dilution sampling apparatus and traditional EPA methods to compare PM_{2.5} mass and chemical speciation. Test plans are presented for a gas turbine facility that will be tested in the fourth quarter of 2002. A preliminary approach for pilot-scale tests is presented that will help define design constraints for a new dilution sampler design that is smaller, lighter, and less costly to use.

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SI UNIT CONVERSION FACTORS

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	<u>English (US) units</u>	X	<u>Factor</u>	=	<u>SI units</u>
Area:	1 ft ²	x	9.29 x 10 ⁻²	=	m ²
	1 in ²	x	6.45	=	cm ²
Flow Rate:	1 gal/min	x	6.31 x 10 ⁻⁵	=	m ³ /s
	1 gal/min	x	6.31 x 10 ⁻²	=	L/s
Length:	1 ft	x	0.3048	=	m
	1 in	x	2.54	=	cm
	1 yd	x	0.9144	=	m
Mass:	1 lb	x	4.54 x 10 ²	=	g
	1 lb	x	0.454	=	kg
	1 gr	x	0.0648	=	g
Volume:	1 ft ³	x	28.3	=	L
	1 ft ³	x	0.0283	=	m ³
	1 gal	x	3.785	=	L
	1 gal	x	3.785 x 10 ⁻³	=	m ³
Temperature	°F-32	x	0.556	=	°C
	°R	x	0.556	=	K
Energy	Btu	x	1055.1	=	Joules
Power	Btu/hr	x	0.29307	=	Watts

Section 1 INTRODUCTION

This project is developing and implementing test technology and methods for characterizing fine particulate emissions from stationary combustion sources used in oil and gas (upstream and downstream) and power generation operations. Emission factors and chemical speciation profiles for several source types are being generated for PM_{2.5} (particles with aerodynamic diameter smaller than 2.5 micrometers) and its precursors including VOC, SVOC, OC/EC, NO_x, SO₂, ammonia, sulfates, nitrates, ammonium, and 40 elements. Previous tests demonstrated that current regulatory methods for fine particulate matter were inadequate, especially when applied to gas-fired sources, and that a dilution sampling technique could provide better source characterization data. Therefore, the project is developing improved dilution sampling technology and methods. The U.S. Department of Energy National Petroleum Technology Office (NPTO), Gas Technology Institute (GTI), American Petroleum Institute (API), California Energy Commission (CEC), the New York State Energy Research and Development Authority (NYSERDA), and GE EER have agreed to cofund the project.

1.1 Motivation for the Project

EPA promulgated new national ambient air quality standards (NAAQS) for PM_{2.5} in 1997. Implementation of the PM_{2.5} NAAQS was delayed for five years to allow collection of ambient air PM_{2.5} data through a national monitoring network and further research into human health risk associated with PM_{2.5}. In 1998, Congress directed EPA to arrange an independent study by The National Research Council (NRC) to identify the most important research priorities & develop a conceptual research plan relevant to setting particulate matter standards. The NRC Committee on Research Priorities for Airborne Particulate Matter identified 1 of the 10 top research priorities for fine particulate studies as "...the characterization of emissions sources...acquisition of emissions data that will be needed to formulate emissions management strategies...measurement method comparisons." Beginning in 2002 states are scheduled to develop State Implementation Plans (SIPs) for achieving the PM_{2.5} NAAQS. States will have three years after non-attainment areas are designated to finalize SIPs. The existing source emissions data needed to do this are far from complete or accurate. The methodology and data

generated in the proposed program will improve the reliability of PM2.5 emission inventories used in source apportionment modeling, and thereby enable industry & regulatory decision makers to develop better PM2.5 attainment strategies.

1.2 Project Approach

The focus of the project includes two main tracks:

- Method Development. The development of dilution tunnel measurement protocols to characterize the size distribution, chemical composition, & emission rates of primary particles & reactive gases that lead to particle formation by atmospheric chemical reactions.
- Source Characterization Tests. Once developed & tested, these measurement methods will have to be applied to a large number of sources to collect the data needed to design successful management strategies. A total of 9 to 12 source tests are planned.

The overall schedule for the project is:

Year 1: Source Characterization (existing dilution system);

Year 2: Method development and source characterization (existing and new dilution systems);

Year 3: Source characterization (new dilution system) and database.

The project approach consists of six tasks (Figure 2-1):

- Task 1 – Method Definition. In this task, GE EER will conduct a series of tests on a pilot-scale combustor to investigate the effect of dilution tunnel design parameters on results under a wide range of simulated source conditions. These results will be used to develop and build a more portable, less costly dilution tunnel design – the next generation of the CalTech design developed in the late 1980's by Hildemann et al. The draft API generic test protocol developed in Phase 1 of the API fine PM project will be revised and updated based on recent test results and developments in sampling technology. The dilution tunnel design and sampling test protocol also will be drafted and proposed to a consensus based standards organization such as ASTM or ASME.
- Task 2 – Source Characterization. This task will provide for field tests on at least six oil & gas industry emission sources. In addition to characterization of source emissions contributing to ambient PM2.5, the tests will be designed to include comparisons of method performance against existing regulatory reference methods. This will provide both new, original data on source emissions

characteristics for different source types and increased acceptance of the test method among the regulatory community. A preliminary “strawman” of sites being considered for testing is provided in Table 1-1. A total of 9 to 11 sources are currently planned, depending on the final test plan for each unit. For selected sites (e.g. gas turbines), tests will include characterization of low load and startup conditions in addition to base load.

Table 1-1. “Strawman” Site Selection.

Combined Cycle plant without Post Combustion NO _x Controls Combined Cycle plant with Post Combustion NO _x Controls Simple Cycle Gas Turbine Combined Cycle plant with supplementary firing Lean Burn Reciprocating Engine Refinery Process Heater with NO _x Controls Refinery Process Vents (FCCU, SRU, CRU) Refinery Process Heater without NO _x Controls Refinery Boiler with NO _x Controls Refinery Combined Cycle Cogen Gas Fired Utility Boiler Residual Oil Fired Utility Boiler Dual-Fuel Fired Commercial Boiler – Albany, New York
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- Task 3 – Data Analysis & Reports. This task will provide for reduction of field and laboratory test results and preparation of project reports. A database of test results from this project and selected external projects also will be developed as the beginning of an industry-specific tool for estimating emissions from industry sources. The database format will be based on the API-WSPA petroleum industry air toxics emission factor database previously developed by GE EER.
- Task 4 – Quality Assurance. It is critical that the quality of the data produced in this project is both known and commensurate with its intended use. This task will provide for quality assurance/quality control activities necessary to accomplish this objective.
- Task 5 – Project Management. This task will provide for DOE project management reports, topical progress reports, and a comprehensive final report on project findings.
- Task 6 – Technology Transfer. For these data to be of greatest benefit for the oil & gas industry, it is important that the results be available in the open literature and that opportunities for peer review of the results are provided. This task will provide for: conference and journal publications; and Ad Hoc Committee meetings of academic, industry, and regulatory agency peers to help guide project direction.

Section 2 EXECUTIVE SUMMARY

This annual report describes the work undertaken in the first year of the project.

Accomplishments during this period include:

- Formation of Ad Hoc Committee of internal and external team members and peer reviewers, and the first meeting thereof in Irvine, California.
- Planning and execution of PM_{2.5} emissions characterization tests on a refinery gas-fired refinery process heater to (a) develop emissions profiles and (b) compare traditional and EPA test methods.
- Planning of PM_{2.5} emissions tests on a natural gas-fired combustion turbine.
- Construction of a second dilution tunnel sampling system to alleviate scheduling conflicts.
- The design of pilot-test studies to assess dilution sampler design criteria was initiated.

Findings

Tests on a refinery gas-fired process heater at a coastal refinery were performed. The main findings from these tests are:

- Primary PM_{2.5} emission factor based on dilution sampling was 0.000037 lb/MMBtu, with an uncertainty of 33 percent.
- The chemical speciation profile of primary PM_{2.5} measured by dilution sampling was 63 percent organic carbon, 11 percent ammonium, 9.1 percent sulfur, 6.6 percent elemental carbon, and the balance among 15 other measured substances.
- Primary PM_{2.5} emissions measured by traditional sampling methods (EPA Methods PRE-4 and 202) were approximately 200 to 600 times (for unpurged and purged impinger trains, respectively) greater than that measured by dilution sampling. On average, 98 percent of the mass from the traditional sampling method was found in the impingers (back half), which is generally defined as submicron condensable particulate matter. Chemical analysis of impinger residues indicates 72 percent of this mass was determined to be sulfates. Based on previous studies, the majority of this sulfate is believed to be due to conversion of gaseous SO₂ to sulfate in the impingers, biasing the results. Further, the filterable (front half) component was found to be near or below the practical quantitation limit for the traditional methods.
- The most prevalent semivolatile organic compounds, a component of organic aerosols, present in the exhaust were naphthalenes. Other compounds were

detected but at much lower levels generally near the minimum detection limits of the method.

- Potential chemical markers for source apportionment “fingerprinting” are sulfate, iron, and zinc.

Conclusions

- Primary PM_{2.5} emissions from gas-fired external combustion sources are extremely low, at or below the practical quantitation limits of traditional test methods.
- Dilution sampling provides more reliable PM_{2.5} mass and chemical speciation emissions from gas-fired external combustion sources for application to analysis of ambient PM_{2.5}, visibility, and health effects impacts.
- Primary PM_{2.5} emissions from external combustion sources are dominated by organic carbon. This may be overstated somewhat due to sampling artifacts that positively bias the organic carbon measurement.
- Condensable PM_{2.5} mass concentration measured using traditional test methods based on hot filters and impinger trains (e.g., US EPA Methods 201A/202) is probably biased high due to artifacts from conversion of gaseous species, especially SO₂, and oversaturation of condensable vapor species compared to the stack plume. Chemical speciation using traditional methods overstates the significance of sulfates due to these artifacts. Therefore, PM_{2.5} source apportionment, visibility impacts, and health risk assessments should be based on data obtained from dilution sampling.
- Because of sampling artifacts, chemical speciation results obtained using dilution sampling methods should never be applied to emission factors obtained using traditional stack test methods.

Section 3 EXPERIMENTAL

3.1 Process Heater Test

The tests were performed on a refinery gas-fired process heater at a refinery referred to in this program as Site 1. The stack serves two heaters: Heater A has a maximum total heat input of 78.9 MMBtu/hr and Heater B has a maximum heat input of 106 MMBtu/hr. Heater A is in service as the fluid catalytic cracking unit (FCCU) feed heater with 48 direct firing pre-mix burners in the firebox. Heater B is in service providing hot oil to heat the unit recovery distillation columns, and utilizes up to 68 burners. Both heaters are natural draft units. Process parameters monitored during testing include: burner gas rate; inlet water rate; steam quality; radiant section, steam and stack temperature; and excess oxygen.

The specific objectives of this test were to:

- Compare PM_{2.5} mass measured using an in-stack filter and iced impinger train (EPA Method PRE-4/202) and mass measured using a dilution tunnel;
- Develop emission factors and speciation profiles for organic aerosols and PM_{2.5} mass;
- Characterize sulfate, nitrate, ammonium, inorganic elements, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media in the dilution sampler;
- Characterize key secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 7 and above; sulfur dioxide (SO₂); and oxides of nitrogen (NO_x); and
- Determine the effect of a post-test nitrogen purge on condensable particulate matter (CPM) results.

3.1.1 Test Overview

The scope of testing is summarized in Table 3-1. The emissions testing included simultaneous collection and analysis of both in-stack and diluted stack gas samples. All emission samples were collected from the stack of the unit. The samples were analyzed for the compounds listed in Table 3-2. Process data and fuel gas samples were collected during the tests to document operating conditions.

Table 3-1. Overview of Sampling Scope for Site 1 Refinery Process Heater Tests.

Sampling Location	Number of Samples		
	Fuel Gas Header	Stack	Ambient Air
EPA Method PRE-4/202 train	--	4	--
EPA Method 17/202 Train	--	4	--
Dilution tunnel Teflon [®] filter Quartz filter K ₂ CO ₃ -impregnated cellulose fiber filter Citric acid-impregnated cellulose fiber filter TIGF/PUF/XAD-4 Tenax Stainless steel canisters DNPH-coated silica gel cartridges	--	4	1
Fuel sample	4	--	--
NO _x , CO, O ₂ , CO ₂	--	Continuous	--
Process monitoring	--	Continuous	--

TIGF - Teflon[®]-impregnated glass fiber filter

PUF - polyurethane foam

XAD-4 - Amberlite[®] sorbent resin

DNPH - dinitrophenylhydrazine

Source Level (In-stack) Samples. In-stack sampling and analysis for filterable (total, PM10 and PM2.5) and condensable particulate matter (CPM) was performed using traditional EPA methods. In-stack cyclones and filters were used for filterable particulate matter.

Dilution Stack Gas Samples. Dilution sampling was used to characterize PM2.5 including aerosols formed in the near-field plume. The dilution sampler (Figure 3-1) extracted a sample stream from the stack into a mixing chamber, where it was diluted approximately 21:1 with purified ambient air. Because PM2.5 behaves aerodynamically like a gas at typical stack conditions, the samples were extracted nonisokinetically. A slipstream of the mixed and diluted sample was extracted into a residence time chamber where it resided for approximately 70 seconds to allow time for low-concentration aerosols, especially organics, to condense and grow.

Table 3-2. Summary of Analytical Targets for Site 1 Refinery Process Heater Tests.

Parameters	In-Stack				Dilution Tunnel								
	Cyclones	Quartz Filter	Impingers	Gases	Quartz Filter	TIGF/ XAD-4	TMF	Tenax	SS Cans	DNPH	K ₂ CO ₃ Filter	Citric acid Filter	Gases
Total PM mass	X	X											
PM10 mass	X	X											
PM2.5 mass	X	X					X						
Condensable particulate mass			X										
Sulfate			X		X								
Chloride			X		X								
Ammonium			X										
Nitrate			X		X								
Elements			X				X						
Organic carbon		X			X								
Elemental carbon		X			X								
Semivolatile organic compounds		X				X							
Volatile organic compounds*								X					
Volatile organic compounds**									X				
Aldehydes										X			
Ammonia (gaseous)												X	
NO _x				X									
SO ₂			X								X		
CO				X									
O ₂				X									
CO ₂				X									
Moisture or relative humidity			X										X
Velocity				X									
Temperature				X									X

TMF = Teflon[®] membrane filterTIGF = Teflon[®]-impregnated glass fiber filter

*Carbon number of 7 or greater

**Carbon number of 2 or greater

The diluted and aged sample then passed through cyclone separators sized to remove particles larger than 2.5 microns, after which samples were collected on various media: high-purity quartz, Teflon[®] membrane (TMF), potassium carbonate-impregnated cellulose fiber, citric acid-impregnated cellulose fiber and Teflon[®]-impregnated glass fiber (TIGF) filters; a polyurethane foam (PUF)/Amberlite[®] sorbent resin (XAD-4)/PUF cartridge to collect gas phase semivolatile organic compounds (SVOCs); Tenax tubes to capture VOCs with a carbon number greater than seven; a stainless steel canister to capture VOCs with a carbon number greater than two; and dinitrophenylhydrazine (DNPH)-coated silica gel cartridges to capture carbonyls (aldehydes). Four samples were collected on four separate test days.

An ambient air sample was collected to establish background concentrations of measured substances. The same sampling and analysis procedures used for the dilution tunnel were applied for collecting ambient air samples.

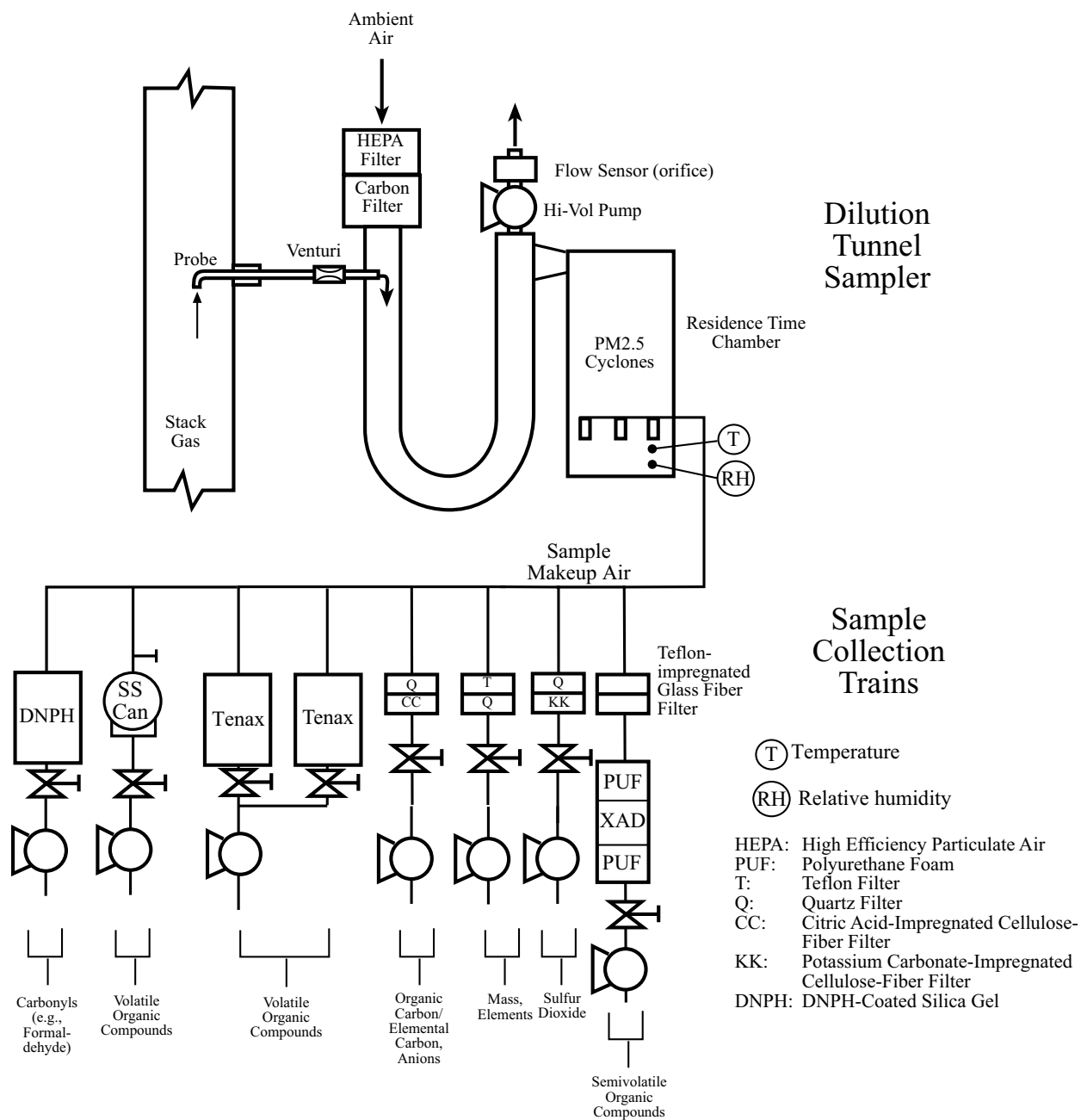


Figure 3-1. Dilution tunnel.

Process Samples. A sample of the fuel gas burned in the process heater was collected on each day of source testing and analyzed for specific gravity, heating value and hydrocarbon speciation.

Sampling and analysis procedures are given in Table 3-3.

Table 3-3. Summary of Test Procedures for Site 1 Refinery Process Heater Tests.

Sampling Location	Measurements	Sampling Approach	Sample Analyses	Reference
S1 (Stack)	Total PM, PM10, PM2.5 and composition	In-stack series cyclones and filter	Mass; organic species	U.S. EPA Method PRE-4 (preliminary method)
	Condensable PM and composition	Impingers	Mass (organic and inorganic), sulfate, chloride, nitrate, ammonium, elements	U.S. EPA Method 202
S1 (Stack)	PM2.5 mass and chemical composition	Dilution tunnel and filters	Mass, organic carbon (OC), elemental carbon (EC), elements, sulfate, nitrate, chloride, ammonium	U.S. EPA, 1999a; Hildemann et al., 1989
	Gaseous PM2.5 precursors	Dilution tunnel and K ₂ CO ₃ -impregnated cellulose-fiber filter	Ammonia	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution tunnel and citric acid-impregnated cellulose-fiber filter	Sulfur dioxide	Chow and Watson, 1998
	VOC	Dilution tunnel and Tenax	Speciated VOC (C7 and greater)	Zielinska et al., 1996; Hildemann et al., 1989
	VOC	Dilution tunnel and stainless steel canisters	Speciated VOC (C2 and greater)	US EPA Method TO-15
	Carbonyls (aldehydes)	Dilution tunnel and DNPH-coated silica gel cartridges	Formaldehyde and other carbonyls	UP EPA Method TO-11A
	SVOC	Dilution tunnel and filter/PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO-13; Hildemann et al., 1989
S2 (Ground level – ambient air)	PM2.5 and chemical composition	Filters	Mass, OC, EC, elements, chloride, sulfate, nitrate, ammonium	U.S. EPA, 1999a
	Gaseous PM2.5 precursors	Dilution tunnel and potassium carbonate-impregnated cellulose-fiber filter	Ammonia	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution tunnel and citric acid-impregnated cellulose-fiber filter	Sulfur dioxide	Chow and Watson, 1998
	VOC	Dilution tunnel and Tenax	Speciated VOC (C7 and greater)	Zielinska et al., 1996; Hildemann et al., 1989
	VOC	Dilution tunnel and stainless steel canisters	Speciated VOC (C2 and greater)	US EPA Method TO-15
	Carbonyls (aldehydes)	Dilution tunnel and DNPH-coated silica gel cartridges	Formaldehyde and other carbonyls	UP EPA Method TO-11A
	SVOC	Dilution tunnel and filter/PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO-13; Hildemann et al., 1989
S3 (Fuel gas feed to heater)	Fuel gas composition	Integrated grab sample (Tedlar bag)	Hydrocarbon speciation, CHON, sulfur content and heating value	ASTM D3588-91

3.2 Gas Turbine Test

Tests will be performed at a cogeneration facility referred to in this program as Site 2. The facility is located in a coastal location on the shore of a large salt water bay. The test unit is a combined cycle generating unit employing a General Electric 7FA gas turbine with steam augmentation. The unit is a single shaft design, with the single generator driven by a shaft common to both the gas and the steam turbines. Hot exhaust gases from the turbine pass through a heat recovery steam generator (HRSG) before venting to the atmosphere via the stack (Figure 3-2). The Vogt HRSG contains supplementary duct burners for additional steam production. The gas turbine's nominal rated base load is approximately 180 MW. The total nominal capacity of the cogeneration facility is 240 MW. The unit will fire natural gas for these tests. The facility is equipped with continuous emissions monitors for CO, O₂ and NO_x. The unit employs GE Mark V Speedtronic® control systems.

The unit was retrofitted with GE's dry low NO_x (DLN) version 2.6 combustion system in February 2000 for NO_x emissions control to 9 ppmv (dry, corrected to 15% O₂) or less over the normal operating load range. The DLN combustion system achieves low NO_x emissions by staging the fuel addition to achieve initial combustion under premixed, fuel-lean conditions. The remaining fuel is added downstream of the premix zone. Design CO concentration is less than 9 ppmv during normal operation. Combustion in the full premixed mode is maintained from 50 to 100 percent of base load.

In addition to DLN, the unit has post-combustion air pollution control equipment. The HRSG is equipped with an oxidation catalyst for control of CO emissions followed by ammonia injection and a selective catalytic reduction (SCR) system for control of NO_x emissions.

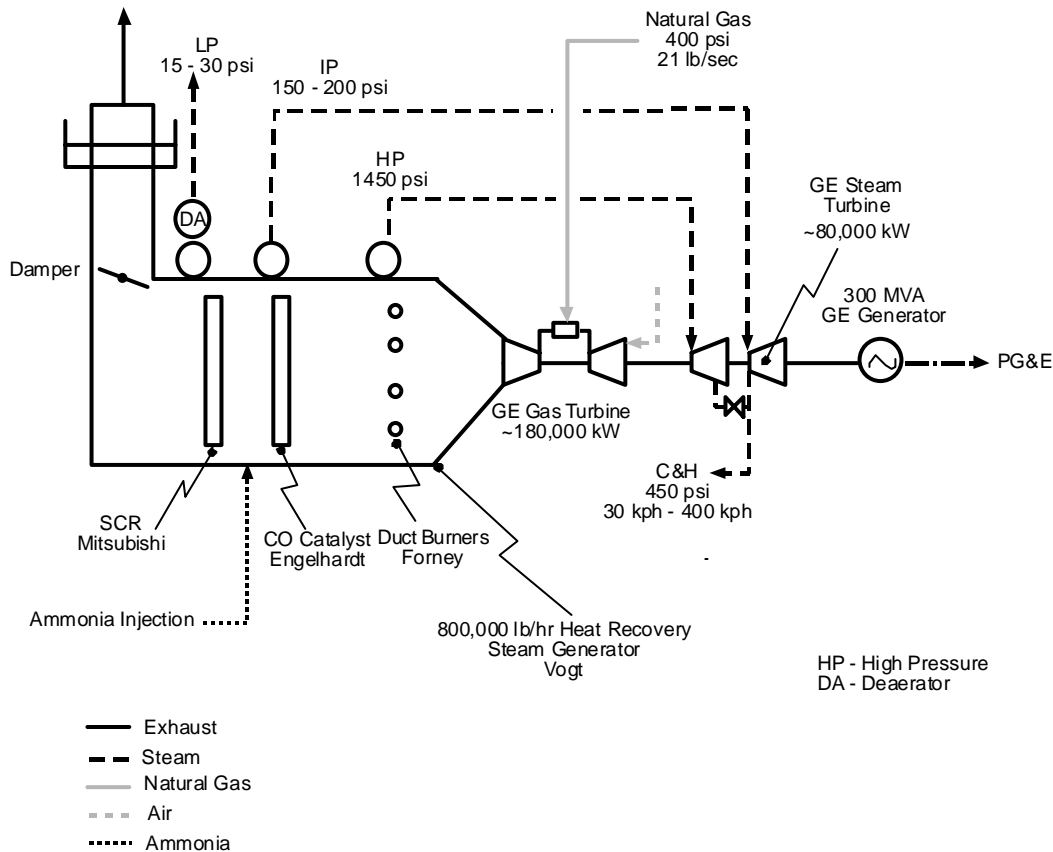


Figure 3-2. Site 2 gas turbine process overview.

The overall goal of this test is to determine PM_{2.5} emissions from a gas turbine and compare results obtained using traditional stack methods and a dilution tunnel method. To this end, the specific objectives of this test project are:

Primary Objectives

- Simultaneously measure emissions at the exhaust stack with a dilution tunnel, EPA Method PRE-4/202 and EPA Method 206 using co-located probes;
- Document pertinent process operating parameters during each test run.
- Compare PM_{2.5} mass measured using an in-stack filter and iced impinger train (EPA Method PRE-4/202) and mass measured using a dilution tunnel;
- Develop emission factors and speciation profiles for organic aerosols and PM_{2.5} mass;
- Characterize sulfate, nitrate, ammonium, inorganic elements, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media in the dilution sampler;

- Characterize key secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 2 and above; sulfur dioxide (SO₂); ammonia (NH₃) and oxides of nitrogen (NO_x); and
- Document the relevant process design characteristics and operating conditions during the test.

Secondary Objective

- Speciate the inorganic condensable PM residue collected using EPA Method 202.

Emissions measurements using EPA manual methods and the dilution tunnel will be performed simultaneously at base load (100 percent of base load to compare the results obtained using the different methods (Table 3-4). Four replicate test runs will be performed. The EPA Method PRE-4/202, EPA Method 206, and dilution tunnel samples will be collected non-isokinetically from a single area in the stacks determined to be the point of average velocity. Previous tests have shown that there is no significant O₂ stratification at the sampling location. A velocity traverse will be performed before and after each test run. CO, NO_x, and O₂ will be monitored during sampling using the plant CEMS. Natural gas composition and heating value will be determined from previous test results and/or natural gas analysis reported by the gas company or plant.

The process parameters that will be monitored during each test run are listed in Table 3-5. At the end of each test day, a hard copy of the process data for the test run time periods will be collected from plant personnel by GE EER.

The unit will be operated at a constant base load during test conditions, as allowed by dispatch requirements. A base load within the range of 75-100 percent of base load is acceptable if a constant 100 percent cannot be maintained. The load should be similar among all test runs.

Table 3-4. Test Matrix for Site 2 Gas Turbine Tests.

Sampling Location	No. of Test Runs (Total)	Sample Type/ Parameter	Sampling/ Test Method	Sampling Organization	Sample Run Time (min)	Analytical Method/ Principle	Analytical Laboratory
Unit Stack	4	Flue Gas/ total PM, PM10, PM2.5 (filterable)	EPA PRE-004 (In-stack cyclones and filter)	GE EER	360	EPA PRE-004/ Gravimetry	GE EER
		Flue Gas/Condensable PM (mass, sulfate, chloride, other ions, elements)	EPA 202 (H ₂ O Impingers)	GE EER	360	EPA 202/ Gravimetry; IC	DRI; Philip Analytical
		Flue Gas/ PM2.5 (mass, OC/EC, elements, ions)	Dilution tunnel (Filter packs)	GE EER	360	Gravimetry, TOR, XRF, IC	DRI
		Flue Gas/ VOC	Dilution tunnel (Tenax)	GE EER	360	GCMS	DRI
		Flue Gas/ VOC	Dilution tunnel (Canister)	GE EER	360	GCFID	DRI
		Flue Gas/ SO ₂	Dilution tunnel (K ₂ CO ₃ filter pack)	GE EER	360	IC	DRI
		Flue Gas/ NH ₃	Dilution tunnel (citric acid filter pack)	GE EER	360	IC	DRI
		Flue Gas/ NH ₃	BAAQMD ST-1B (HCl impingers)	GE EER	360	ISE	CalScience
		Flue Gas/ aldehydes	Dilution tunnel (DNPH cartridges)	GE EER	360	HPLC	DRI
		Flue Gas/ SVOC	Dilution tunnel (TIGF/ PUF/ XAD)	GE EER	360	GCMS	DRI
Ambient Air (Combustion inlet)	1	Ambient/ PM2.5 (mass, OC/EC, elements, ions)	Dilution tunnel (Filter packs)	GE EER	360	Gravimetry, TOR, XRF, IC	DRI
		Ambient/ VOC	Dilution tunnel (Tenax)	GE EER	360	GCMS	DRI
		Ambient/ VOC	Dilution tunnel (Canister)	GE EER	360	GCFID	DRI
		Ambient/ SO ₂	Dilution tunnel (K ₂ CO ₃ filter pack)	GE EER	360	IC	DRI
		Ambient/ NH ₃	Dilution tunnel (citric acid filter pack)	GE EER	360	IC	DRI
		Ambient/ aldehydes	Dilution tunnel (DNPH cartridges)	GE EER	360	HPLC	DRI
		Ambient/ SVOC	Dilution tunnel (TIGF/ PUF/ XAD)	GE EER	360	GCMS	DRI

CEMS: continuous emissions monitoring system

DNPH: dinitrophenylhydrazine

GCMS: gas chromatography/ mass spectrometry

HPLC: high performance liquid chromatography

IC: ion chromatography

ICP-MS: inductively coupled plasma-mass spectrometry

ISE: ion selective electrode

PUF: polyurethane foam

TIGF: Teflon impregnated glass fiber filter

TOR: thermal-optical reflectance

XAFS: x-ray absorption fine structure spectroscopy

XRD: x-ray diffraction

XRF: x-ray fluorescence

Table 3-5. Process Operating Data to be Collected During Test Runs for Site 2 Gas Turbine Tests.

Parameter	Location	Point Name	Monitoring Station	Units	Frequency
Natural gas flow rate	Fuel flow meter			lb/sec	Every 10 minutes
Gas turbine generator output (gross)	TBD			MWe	Every 10 minutes
Combustion reference temperature	TBD		Calculated	°F	Every 10 minutes
Extraction steam flow	TBD			lb/hr	Every 10 minutes
Process steam pressure	TBD			psig	Every 10 minutes
Process steam temperature	TBD			°F	Every 10 minutes
Condenser return temperature	TBD			°F	Every 10 minutes
Condenser return flow	TBD			GPM	Every 10 minutes
Steam flow to C&H	TBD			lb/hr	Every 10 minutes
Ambient humidity	TBD			%RH	Every 10 minutes
Ambient barometric pressure	TBD			in. Hg	Every 10 minutes
Ambient dry bulb temperature	TBD			°F	Every 10 minutes
Gas turbine exhaust (HRSG inlet) temperature	TBD			°F	Every 10 minutes
Gas turbine compressor inlet pressure	TBD			in H ₂ O	Every 10 minutes
Gas turbine compressor discharge (combustor inlet) pressure	TBD			psig	Every 10 minutes
Gas turbine compressor inlet temperature	TBD			°F	Every 10 minutes
Compressor inlet specific humidity	TBD			lb H ₂ O/lb air x 10 ⁻³	Every 10 minutes
Gas turbine compressor discharge (combustor inlet) temperature	TBD			°F	Every 10 minutes
Gas turbine exhaust pressure	TBD			in. Hg	Every 10 minutes
Gas flow to HRSG	TBD			lb/hr	Every 10 minutes
HRSG stack outlet temperature	TBD			°F	Every 10 minutes
HRSG stack O ₂	Stack			%	Every 10 minutes
HRSG stack NO _x	Stack			ppm	Every 10 minutes
HRSG stack CO	Stack			ppm	Every 10 minutes
CO catalyst inlet temperature	TBD			°F	Every 10 minutes
HRSG NH ₃ supply flow	TBD			lb/hr	Every 10 minutes
Fuel heat content	GC			Btu/scf	Every 10 minutes
Fuel specific gravity	GC			--	Every 10 minutes

*Document any operating or maintenance problems that may impact emissions or gas turbine performance

Figure 3-3 presents the planned schedule of testing. Test runs will be 6 hours long and will be performed at base load (100 percent of base load). Note, the tests were postponed several times due to plant dispatch requirements and are now planned for early September 2001; however, this

may change pending further developments. The tests will be scheduled to ensure that the units can operate at the same load for the required duration of the tests.

Date	4-Sep													5-Sep												
Time of Day	7	8	9	10	11	12	13	14	15	16	17	18	19	7	8	9	10	11	12	13	14	15	16	17	18	19
Normal Disptach																										
Base Load*																										

Date	6-Sep													7-Sep												
Time of Day	7	8	9	10	11	12	13	14	15	16	17	18	19	7	8	9	10	11	12	13	14	15	16	17	18	19
Normal Disptach																										
Base Load*																										

Date	8-Sep													9-Sep												
Time of Day	7	8	9	10	11	12	13	14	15	16	17	18	19	7	8	9	10	11	12	13	14	15	16	17	18	19
Normal Disptach																										
Base Load*																										

Date	10-Sep													11-Sep												
Time of Day	7	8	9	10	11	12	13	14	15	16	17	18	19	7	8	9	10	11	12	13	14	15	16	17	18	19
Normal Disptach																										
Base Load*																										

* Ideally, 100% of base load. Load should be as constant as possible during testing within the constraints set by dispatch. Target is 75-100% of base load.

Figure 3-3. Planned plant operating schedule for Site 2 gas turbine tests.

3.3 Dilution Tunnel Design Assessment Tests

One goal of this program to experimentally understand and quantify equipment design criteria for characterizing PM_{2.5} and precursor emissions from stationary sources by means of dilution sampling methods. Results from previous test programs using the current dilution tunnel design proved the feasibility of dilution sampling for stationary sources and drawbacks of the current design. The key issues are:

- The physical size of the dilution sampler, consisting of the dilution tunnel and residence time chamber, is large. This limits its application to stacks with adequately large and sturdy sampling platforms. It also makes traversing the sampling probe across the stack cross-section impractical. Setup is time consuming and the weight is an inconvenience to raising the equipment onto elevated sampling platforms.

- Operation is complex, requiring highly trained operating personnel to obtain satisfactory results.
- Losses of particles in the dilution tunnel and residence time chamber are unknown for different applications. One test on a unit with high solid and condensable particle concentrations showed significant loss of solid particles in the probe, and to a lesser but undefined degree in the dilution tunnel.
- Optimum dilution ratio for different concentrations of particles and particle types is unknown.
- The effect of residence time is unknown.

In Task 1, the effects of various dilution tunnel design and operating parameters on measured PM will be assessed experimentally in a pilot-scale combustion rig. Preliminary planning for these tests was initiated during this reporting period.

The effects of different dilution sampler operating conditions, i.e., dilution air ratio, residence time, for different source types (e.g. fuel types, condensable PM loading, solid PM loading) on measured PM_{2.5} concentration will be evaluated at the Fuel Evaluation Facility (FEF) at GE EER's test site in Irvine, CA. The results of this study will be used to design the next generation dilution sampler.

The pilot test objectives are:

- Quantify PM_{2.5} mass and ultrafine particle number size distributions via dilution sampling from FEF for combustion of natural gas, residual oil and coal.

The key questions regarding design of the sampler are

- How does residence time affect the PM_{2.5} mass and number distributions of ultrafine particles?
- How does the dilution ratio affect PM_{2.5} mass and number distributions ultrafine particles?
- How does the minimum residence time and dilution ratio for stable mass and size distribution vary for different fuel?

Other questions are:

- How do stack temperature and relative humidity affect the accuracy of PM_{2.5} measurements?
- How does the mixing rate of dilution flow affect PM_{2.5} measurements?

- How does PM_{2.5} emission rate at the test facility compared to emission rate at individual facilities?

A phased test program was conceived to facilitate review of initial results prior to completing the entire test program:

- Phase I Screening Tests – an initial series of tests to investigate the effects of dilution ratio and residence time will be conducted on the pilot combustor firing natural gas, residual fuel oil, and coal. These fuels produce stack gases that represent extremes of solid and condensable aerosol concentrations. The tests will also validate the feasibility of using a scanning mobility particle sizer (SMPS), which employs a differential mobility analyzer and a condensation nuclei counter in series to measure ultrafine particle size distribution, to characterize aerosol stability.
- Phase II Screening Tests – these tests will complete the screening of dilution tunnel design parameters after the feasibility of the SMPS has been established.
- Phase III Parametric and Comparison Tests – these tests will focus on tests using the new dilution sampler designed in this program and compare results from different dilution sampler designs in the pilot scale combustor. The focus of this series is to validate design criteria by direct manipulation of design parameters and comparison of results obtained from very different designs.

The exact plan for the tests in each phase are still under development at the end of this reporting period. However, the main thrust of the tests is described below.

The current dilution tunnel sampler (Figure 3-4), which was developed by DRI based on the designs of Hildemann et al. (1989) will be deployed to collect exhaust gas samples from the pilot-scale combustor (Figure 3-5). The combustor will be operated at a nominal heat input rate of 160kW and 3% excess oxygen. The dilution sampler withdraws the stack gas sample at a rate of approximately 25 liters per minute from a single point approximately in the center of the 6-inch inside diameter stack. A PM_{2.5} cyclone inlet will be attached to a stainless steel probe with a buttonhook nozzle, which is used to limit the entry of coarse particle into the dilution chamber. The sample flow rate through the probe will be monitored using a venturi flow meter and thermocouple. The venturi velocity head is measured continuously during the test with a Magnehelic gauge. The thermocouples and pressure transducers are connected to a laptop computer data acquisition system.

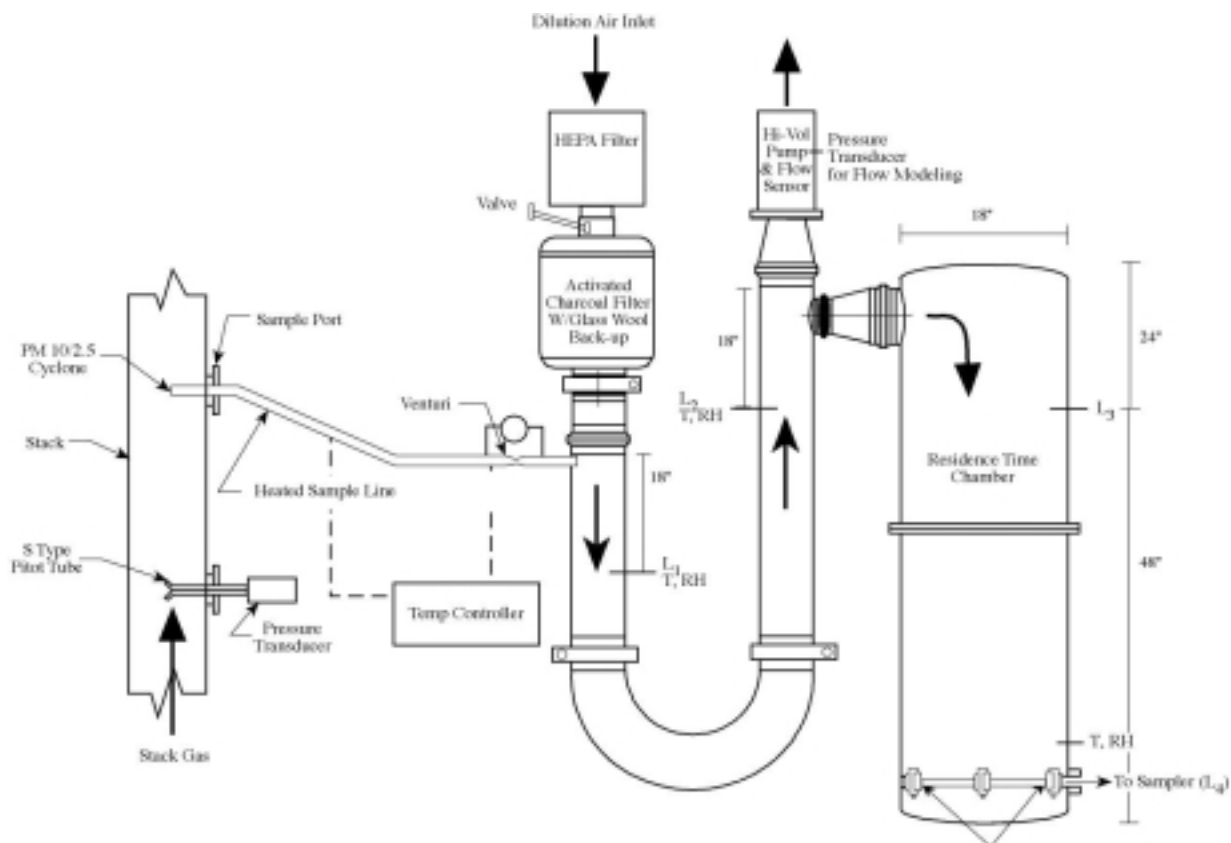


Figure 3-4. Current generation dilution sampler developed by DRI based on designs by Hildemann et al. (Chow et al.).

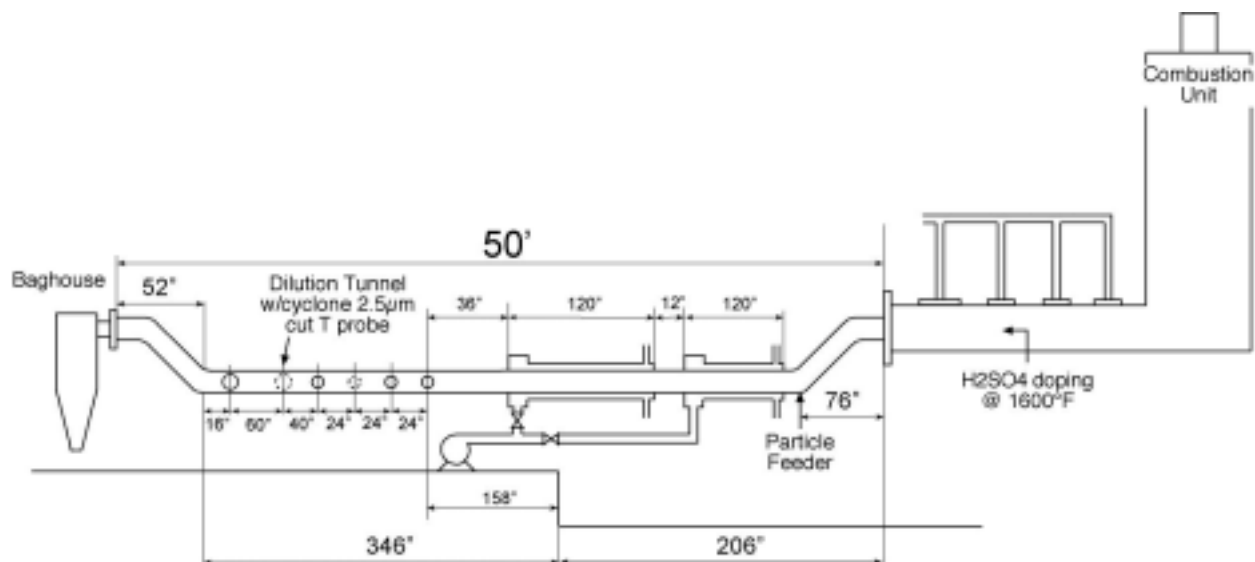


Figure 3-5. Pilot-scale fuels evaluation furnace.

Table 3-6 shows testing matrix to simulate PM emitted at actual plume conditions as a function of dilution air ratio, residence time at different fuel types and flue gas temperatures. Diluted samples will be extracted from the dilution tunnel and residence time chambers at locations corresponding to 2, 10 and 80 seconds residence time at each of two dilution ratios. Because particles will continue interacting with surrounding substances once particles are emitted to the atmosphere and depends on its lifetime (hours and days), dilution sampling only approximates the early aerosol formation process. The goal of the tests will be to define the minimum residence time needed for particle condensational growth for different dilution ratios and stack gas conditions, commensurate with minimal particle diffusive wall losses.

Table 3-6. Testing Matrix of Dilution Sampler to Simulate PM Emitted from Actual Plume Condition

Testing Parameters	Condition		
Particle Residence Time	2 second	10 second	80 second
Dilution Ratio	10 X	50 X	
Fuel Type	Natural Gas	#6 heating oil	Kittanning coal
Flue gas temperature	450°K	645°K	

Dilution ratios of 10 and 50 times will be evaluated as these represent reasonable extremes based on prior studies. At the 10X dilution ratio, the locations of 2, 10 and 80 second residence time corresponding to L1, L2, and L4, and L2, L3, L4 for 50 times dilution ratio respectively (Figure 3-4). The dilution airflow and backpressure will be adjusted to maintain the target dilution ratio and sample flow rates.

Three different fuel types, natural gas, #6 heating oil and Kittanning coal will be used in the tests to examine the applicability of dilution technology in different PM source levels. In addition, during natural gas combustion, some tests will be conducted with doping of sulfuric acid to simulate formation of condensable acid aerosols in a flue gas free from solid particles. A dilute solution of sulfuric acid will be atomized into the furnace at a flue gas temperature of approximately 1144°K (1600°F), at which sulfuric acid should rapidly decompose to form SO₃

but not SO₂. Also, the effect of flue gas temperature on PM formation will be evaluated at temperatures of approximately 450±10°K and 645±10°K.

The sample collection media that will be used in dilution sampler are listed in Table 3-7. At each residence time sampling port, a total of 30 L min⁻¹ will be drawn through a 3/8" tube and split to two parallel 47mm filter holders (one pre-weighed PTFE filter and one pre-baked 47mm quartz filter) at 15 L min⁻¹ each. Samples will be collected for 2-6 hours, depending on the nature of test fuel type, to obtain a detectable sampling loading. The filters will be analyzed for mass and elemental, metal, ion and carbon content (depending on the type of tests). The results of these measurements will be paired and normalized to determine particle growth and potential particle losses in dilution sampler. In addition, a DustTrak, light scattering detector (model 8520, TSI), and a Scanning Mobility Particle Sizer (DMA model 3071 and CPC model 3025, TSI) will be used to provide real-time readouts during sampling. The DustTrak samples at 1.7 L min⁻¹ with a PM_{2.5} inlet and will be connected to the 80 second residence time sampling port. The DustTrak estimates the real time particle mass concentration. SMPS measures the real time particle number distribution for the 0.01-0.4mm size range and samples 5 minute average interval from the 2, 10 and 80s residence time locations. The SMPS measurement will be repeated through the test. These real time measurements will be used to quantify the changes of particle mass and size distribution throughout the test.

A modified Micro-Orifice Uniform Deposit Impact (Marple, 1981) with stages for <0.32 mm and 0.32-2.5 mm size range samples at 30 liters per minute at the outlet of sampler (corresponding to 80 second residence time) to collect ultrafine particles in two size fractions (less than 0.32mm and in the accumulation mode 0.32-2.5 mm) for analysis of mass, elements and metals content.

Table 3-7. Samplers Used to Characterize PM_{2.5} Formation in Dilution Sampler.

Type of media	Type of analysis	Residence time (s)
Quartz filters	TOR (EC and OC) IC (nitrate, ammonia, chloride)	2, 10 and 80
47mm PTFE filters	Gravimetric (mass concentration) XRF (metals and elements)	2, 10 and 80
Scanning Mobility Particle Sizer (SMPS)	Ultrafine (0.01-0.4 μ m) particle size distribution	Shifting among 2, 10 and 80 seconds then taking the average of PSD at given residence time
DustTrak model 8520	Real time particle mass concentration	80 second
Micro-Orifice Uniform Deposit Impactor	Size segregated mass, elements and metals in size range <0.32, 0.32-2.5 μ m	80 second

Section 4 RESULTS AND DISCUSSION

4.1 Site 1 Refinery Process Heater Test Results

Test results from the Site 1 Refinery Process Heater tests were completed during this reporting period. All stack emission results are presented in units of milligrams per dry standard cubic meter (mg/dscm) and pounds per hour (lb/hr). Concentrations are corrected to a standard temperature of 68°F and a standard pressure of 29.92 inches of mercury unless otherwise indicated. See the conversion factors presented at the beginning of this report to convert to SI units. Substances that were not detected in any of the four test runs generally are not listed on the tables. Where shown, undetected data are flagged “ND”, treated as zeroes in sums, and excluded from average calculations. The approximate minimum in-stack detection limits achieved for all measured substances are given in Table 4-1.

4.1.1 Process Operating Conditions

Heater operating conditions during testing are summarized in Table 4-2. The process heater operated at close to its normal firing rate corresponding to approximately 90 percent of full firing capacity.

The average fuel higher heating value (HHV) during each test was obtained from the plant process data. The average heat input to the process heater during the test is the product of the average fuel-gas flow rate and the average fuel HHV. The average heat input was used to convert in-stack emission rates (lb/hr) to emission factors (lb/MMBtu), which are presented in Section 5. Results of the analysis of the fuel gas, as determined from grab samples taken during each run, are presented in Table 4-3. Total reduced sulfur content of the fuel (as H₂S) was approximately 200 part per million by volume (ppmv) on average, with H₂S comprising only 2.8 ppmv (Table 4-4).

4.1.2 Preliminary Tests

Preliminary tests were conducted to establish a single point in the stack for sample collection. A velocity profile was developed by traversing the stack with the pitot probe before and after each

test. The resulting average velocity profile was used to correct the velocities measured at the center during sampling to the overall stack average velocity.

Table 4-1. Approximate In-Stack Detection Limits Achieved for Gas-Fired Process Heater Tests (Site 1).

Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm	Substance	Dilution Tunnel mg/dscm	Substance	Dilution Tunnel mg/dscm	Substance	Dilution Tunnel mg/dscm
Total PM mass	--	2.5E-03	Sr	1.3E-05	2-methylnaphthalene	7.1E-05	Benzo(b)chrysene	2.2E-06
PM10 mass	--	2.5E-03	Ti	3.6E-05	2-methylphenanthrene	2.2E-06	Benzo(b+j+k)fluoranthene	1.1E-06
PM2.5 mass	9.5E-04	2.5E-03	Tl	3.1E-05	2-phenylnaphthalene	1.1E-06	Benzo(c)phenanthrene	1.2E-05
Ag	1.5E-04	--	U	2.8E-05	3,6-dimethylphenanthrene	5.3E-05	Benzo(e)pyrene	6.9E-06
Al	1.2E-04	--	V	3.1E-05	3-methylbiphenyl	2.5E-04	Benzo(ghi)perylene	6.7E-06
As	2.0E-05	--	Y	1.6E-05	4-methylbiphenyl	2.1E-05	Benzonaphthothiophene	2.2E-06
Au	3.8E-05	--	Zn	1.3E-05	4-methylpyrene	2.2E-06	Bibenzene	2.8E-03
Ba	6.4E-04	--	Zr	2.1E-05	4H-cyclopenta(def)phenanthrene	0.0E+00	Biphenyl	7.5E-05
Br	1.2E-05	--	SO4=	1.4E-03	5+6-methylchrysene	0.0E+00	C-dimethylphenanthrene	3.7E-05
Ca	5.5E-05	--	NO3-	1.4E-03	7-methylbenz(a)anthracene	6.9E-06	C-methylphenanthrene	3.1E-05
Cd	1.5E-04	--	NH4+	--	7-methylbenzo(a)pyrene	7.9E-06	C-trimethylnaphthalene	9.0E-06
Cl	1.2E-04	--	Cl-	1.4E-03	9,10-dihydrobenzo(a)pyrene	3.4E-06	Cholestane	3.0E-04
Co	1.1E-05	--	OC	1.1E-02	9-anthraldehyde	3.0E-05	Chrysene	2.2E-06
Cr	2.3E-05	--	EC	2.5E-03	9-fluorenone	1.5E-04	Coronene	6.7E-06
Cu	1.3E-05	--			9-methylanthracene	5.2E-05	D-dimethylphenanthrene	3.4E-05
Fe	1.8E-05	--	1+2-ethylnaphthalene	1.4E-04	A-dimethylphenanthrene	5.3E-05	D-MePy/MeFl	1.1E-06
Ga	2.3E-05	--	1,2,8-trimethylnaphthalene	6.7E-06	A-methylfluorene	1.2E-04	Dibenz(ah+ac)anthracene	6.7E-06
Hg	3.2E-05	--	1,2-dimethylnaphthalene	7.8E-05	A-methylphenanthrene	5.4E-05	Dibenzofuran	7.0E-05
In	1.6E-04	--	1,3+1,6+1,7-dimethylnaphthalene	2.6E-04	A-methylpyrene	1.1E-06	E-dimethylphenanthrene	1.7E-05
K	7.5E-05	--	1,4+1,5+2,3-dimethylnaphthalene	1.1E-04	A-trimethylnaphthalene	2.1E-06	E-MePy/MeFl	1.1E-06
La	7.6E-04	--	1,4,5-trimethylnaphthalene	1.1E-04	Acenaphthene	2.9E-05	E-trimethylnaphthalene	1.1E-06
Mg	0.0E+00	--	1,4-chrysenequinone	5.6E-06	Acenaphthenequinone	6.7E-06	F-trimethylnaphthalene	1.1E-06
Mn	2.0E-05	--	1,7-dimethylphenanthrene	3.7E-05	Acenaphthylene	1.2E-04	Fluoranthene	2.2E-06
Mo	3.3E-05	--	1,8-dimethylnaphthalene	7.8E-05	Anthracene	1.1E-06	Fluorene	1.4E-04
Na	0.0E+00	--	1-ethyl-2-methylnaphthalene	2.2E-06	Anthraquinone	0.0E+00	Indeno[123-cd]pyrene	6.7E-06
Ni	1.1E-05	--	1-MeFl+C-MePy/Fl	1.8E-05	Anthrone	6.1E-05	J-trimethylnaphthalene	9.0E-06
P	6.9E-05	--	1-methylfluorene	7.4E-05	B-dimethylphenanthrene	3.7E-05	Naphthalene	1.1E-03
Pb	3.7E-05	--	1-methylnaphthalene	4.3E-05	B-MePy/MeFl	1.1E-06	Perinaphthenone	1.1E-03
Pd	1.3E-04	--	1-methylphenanthrene	2.5E-05	B-methylfluorene	7.4E-05	Perylene	2.2E-06
Rb	1.2E-05	--	1-methylpyrene	9.0E-06	B-methylphenanthrene	1.2E-05	Phenanthrene	9.0E-06
S	6.1E-05	--	1-phenylnaphthalene	5.6E-06	B-trimethylnaphthalene	1.1E-06	Pyrene	4.5E-06
Sb	2.2E-04	--	2,3,5+1-trimethylnaphthalene	3.4E-06	Benz(a)anthracene	6.7E-06	Retene	6.7E-05
Se	1.5E-05	--	2,4,5-trimethylnaphthalene	9.0E-06	Benz(a)anthracene-7,12	4.2E-05	Xanthone	4.5E-06
Si	7.7E-05	--	2,6+2,7-dimethylnaphthalene	1.2E-04	Benzanthrone	1.0E-05	Volatile Organic Compounds	3.0E-02
Sn	2.1E-04	--	2-ethyl-1-methylnaphthalene	1.9E-04	Benzo(a)pyrene	6.7E-06		
			2-methylbiphenyl	1.8E-04				

Table 4-2. Process Operating Conditions (Site 1).

Parameter	Units	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01
Total fuel gas flow	scfh	129,474	135,448	136,267	143,685
Heater A feed rate	bph	1393	1301	1384	1404
Heater B feed rate	bph	2016	2402	2402	2402
Heater A outlet temperature	°F	695	705	695	700
Heater B outlet temperature	°F	658	712	909	716
Fuel heat content (HHV)	Btu/ft ³	1218	1231	1185	1168
Fuel specific gravity	--	0.80	0.77	0.78	0.76
O ₂	%	8.9	8.6	8.9	8.2
CO	ppm	0.5	1.0	0.5	21
NO _x	ppm	77	93	85	83
Heat Input (1)	MMBtu/hr	158	167	161	168

(1) Calculated from the fuel heat content and the fuel flow rate.

Table 4-3. Fuel Gas Analysis (Site 1).

Date	Units	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01	Average	RSD (%)
Specific Gravity	None	0.847	0.923	0.825	0.837	0.858	5.2
Gross Btu	Btu/cu. ft.	1294	1368	1252	1276	1298	3.9
Dry F Factor ¹	sdcf/MMBtu	7740	7640	7760	7669	7702	0.7

Methane	%	39.1	30.2	41.3	37.2	37.0	13.0
Ethane	%	9.7	9.7	9.9	9.8	9.8	1.0
Ethylene	%	3.5	3.4	3.7	3.4	3.5	4.0
Propane	%	10.0	8.8	4.5	8.9	8.1	30.2
Propylene	%	2.9	5.5	6.0	4.4	4.7	29.2
i-Butane	%	1.3	3.3	1.3	1.1	1.8	59.3
n-Butane	%	5.4	4.8	4.9	4.7	5.0	6.3
1-Butene	%	0.2	0.6	0.2	0.2	0.3	66.7
2-Methyl Butane	%	ND	0.9	0.2	0.2	0.4	93.3
i-Pentane	%	1.0	1.9	0.9	0.9	1.2	41.3
n-Pentane	%	0.5	0.8	0.5	0.5	0.6	26.1
1-Pentene	%	0.1	0.1	0.1	0.1	0.1	0.0
2,2-Dimethyl Butane	%	0.1	0.1	0.1	0.1	0.1	0.0
2,3-Deimethyl Butane	%	0.1	0.1	0.1	0.1	0.1	0.0
2-Methyl Pentane	%	0.1	0.1	0.1	0.1	0.1	0.0
3-Methyl Pentane	%	0.1	0.1	0.1	0.1	0.1	0.0
n-Hexane	%	0.1	0.1	0.1	0.1	0.1	0.0
1-Hexene	%	ND	0.1	0.1	0.1	0.1	0.0
C ₆ +	%	0.1	0.0	0.1	0.1	0.1	66.7
CO ₂	%	0.2	0.1	0.2	0.1	0.2	38.5
CO	%	0.5	0.5	0.5	0.6	0.5	9.5
O ₂	%	1.8	2.2	1.8	1.6	1.9	13.6
N ₂	%	7.5	8.9	8.0	8.1	8.1	7.1
H ₂	%	15.9	17.7	15.3	17.4	16.6	7.0
H ₂ S	%	<0.1	<0.1	<0.1	<0.1	<0.1	0.0
Total		100	100	100	100	100	

(1) Dry F Factor at 68 F and 1 atm (ASTM 3588).

Table 4-4. Fuel Gas Sulfur Speciation Results (Site 1).

Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01	Average	RSD (%)
Time	14:37	16:52	13:10	12:30		
H ₂ S	2.5	2.3	3.1	3.4	2.8	18
Carbonyl Sulfide	12.6	15.5	12.3	13.4	13.5	11
Methyl Mercaptan	67	138	76.2	67.6	87.2	39
Ethyl Mercaptan	23.8	35.6	30.6	27.8	29.5	17
Unidentified Sulfur Compounds	60.8	73.8	65.5	61.4	65.4	9
Total Reduced Sulfur as H ₂ S	167	265.3	188	174	199	23

4.1.3 Stack Gas Conditions and Flow Rate

A summary of the stack conditions during testing is presented in Table 4-5. Stack gas temperature during the tests averaged 744-806°F.

Table 4-5. Average Stack Conditions (Site 1).

Parameter	Units	Run 1	Run 2	Run 3	Run 4
Date		15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01
Stack Temperature	°F	771	744	798	806
Moisture	%v	11	11	11	12
Velocity	ft/s	26	25	26	25
	m/s	8.0	7.7	8.0	7.5
Flow Rate	acfm	150,900	144,900	150,600	141,800
	dscfm	57,800	56,800	56,600	52,000
	dscmm	1,600	1,600	1,600	1,500

4.1.4 In-Stack and Impinger Method Results

Particulate Mass

Filterable particulate matter (FPM). Filterable particulate matter (FPM) results as measured by Method PRE-4 are presented in Table 4-6. Total FPM, which includes all particulate collected in the in-stack nozzle/cyclone assembly and on the in-stack filter, ranged from 0.17 to 1.01 mg/dscm. FPM < 10 micrometers, which includes the portion of total FPM collected downstream of the PM10 cyclone, was 0.17 to 0.69 mg/dscm. FPM < 2.5 micrometers, which includes the portion of FPM collected downstream of the PM2.5 cyclone and on the in-stack filter, was 0.12 to 0.49 mg/dscm. These in-stack concentrations correspond to total weight gains in the sampling train of 0.7 to 4 milligrams (mg), with uncorrected net weights in each fraction of –1.6 to 1.7 mg. This result reflects the extremely low particulate loading in the stack and suggest that the particulate mass loading at the stack in these tests may be near or below the practical limits of the overall method.

Table 4-6. Filterable Particulate Matter Results (Site 1).

Parameter	Units	Results					
Run Number	-	1	2	3	3	Average	RSD
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		
Total FPM	mg/dscm	0.68	< 1.01	< 0.17	1.01	< 0.72	55%
(by Method PRE-4)	lb/hr	1.5E-1	< 2.1E-1	< 3.5E-2	2.1E-1	< 1.5E-1	55%
Total FPM	mg/dscm	< 0.39	0.38	< 0.56	< 0.40	< 0.43	19%
(by Method 17)	lb/hr	< 8.4E-2	7.9E-2	< 1.2E-1	< 7.8E-2	< 9.0E-2	23%
FPM <10 µm	mg/dscm	0.49	< 0.54	< 0.17	0.69	< 0.47	47%
(by Method PRE-4)	lb/hr	1.1E-1	< 1.1E-1	< 3.5E-2	1.4E-1	< 1.0E-1	46%
FPM <2.5 µm	mg/dscm	0.49	< 0.38	< 0.12	0.39	< 0.34	46%
(by Method PRE-4)	lb/hr	1.1E-1	< 8.1E-2	< 2.5E-2	8.1E-2	< 7.3E-2	47%

<-one or more, but not all, constituents are less than the detection limit

RSD-relative standard deviation

Total FPM as measured by Method 17 is also shown in Table 4-6. The total FPM as measured by the two different methods is on the same order of magnitude.

Condensable Particulate Matter (CPM). Since there has been much comment on the effect of a post-test nitrogen purge on the levels of CPM collected in the Method 202 impingers, two separate trains were sampled simultaneously, as described in Section 3, with one being purged after sampling was completed and the other not undergoing a purge. It was expected that the purged train would show lower CPM and sulfate levels, however the reverse is indicated by the results. No The results are summarized in Table 4-7.

Purged Train. The average total CPM, which is the sum of the evaporated organic extract, the inorganic residue (corrected for addition of NH₄OH) and the back-half filter, is 18.9 mg/dscm. The total inorganic mass is 17.4 mg/dscm, 80 percent of which is accounted for by sulfate, with a concentration of 13.9 mg/dscm. This sulfate concentration is determined from the aliquot taken from the impinger catch and rinse before it is extracted with the organic solvent. The average organic CPM concentration is 1.3 mg/dscm. This result is higher than previous tests on a gas-fired boiler, gas-fired heater and gas-fired steam generator that had organic CPM concentrations of 0.6, 0.2 and 0.8 mg/dscm, respectively.

Table 4-7. Condensable Particulate Matter (Method 202) Results (Site 1).

Parameter	Units	Value					
Run Number	-	1	2	3	3	Average	RSD
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		
Inorganic CPM (Purged Train) (1)	mg/dscm	24.7	11.9	13.6	19.5	17.4	34%
	lb/hr	5.4	2.5	2.9	4.1	3.7	35%
Inorganic CPM (Unpurged Train)	mg/dscm	7.5	0.8	7.3	4.9	5.1	74%
	lb/hr	1.6	0.2	1.5	0.9	1.1	76%
Organic CPM (Purged Train)	mg/dscm	1.1	1.1	1.7	1.2	1.3	24%
	lb/hr	0.2	0.2	0.4	0.3	0.3	24%
Organic CPM (Unpurged Train)	mg/dscm	1.3	0.5	0.9	0.5	0.8	50%
	lb/hr	0.3	0.1	0.2	0.1	0.2	53%
Sulfate (as SO ₄ ⁻) in Impingers (Purged Train)	mg/dscm	18.7	10.7	10.6	15.6	13.9	29%
	lb/hr	4.1	2.3	2.2	3.3	3.0	29%
Sulfate (as SO ₄ ⁻) in Impingers (Unpurged Train)	mg/dscm	5.8	3.0	5.8	4.4	4.7	29%
	lb/hr	1.3	0.6	1.2	0.9	1.0	31%
Total CPM (Purged Train) (corrected for NH ₄ ⁺ and H ₂ O)	mg/dscm	26.4	< 12.9	15.5	20.9	< 18.9	32%
	lb/hr	5.7	< 2.7	3.3	4.4	< 4.0	33%
Total CPM (Unpurged Train) (corrected for NH ₄ ⁺ and H ₂ O)	mg/dscm	< 8.8	< 1.3	8.4	5.5	< 6.0	70%
	lb/hr	< 1.9	< 0.3	1.8	1.1	< 1.3	72%

RSD-relative standard deviation

CPM-condensible particulate matter

<-one or more, but not all, constituents are less than the detection limit

(1) Purged Train: one-hour post-test nitrogen purge performed; Unpurged Train: no purge performed.

CPM concentration was approximately 50 times greater than FPM2.5 on average. On average, approximately 92 percent of the CPM was found in the inorganic fraction, while 7 percent was found in the organic fraction; the remaining mass is accounted for in the impinger filter that is not speciated. The inorganic and organic CPM results are somewhat variable from run to run, with standard deviations equal to 34 and 24 percent of the average result, respectively. CPM results have been corrected for dichloromethane and water recovery blank results. The data are also corrected for ammonium ion retained and combined water released in the acid base titration, as described in Method 202. Further discussion of the data is provided in Section 7.

Unpurged Train. The average total CPM concentration is 6.0 mg/dscm and the average inorganic CPM concentration is 5.1 mg/dscm, both approximately three times lower than that determined from the Purged Train. The average organic CPM is 0.8 mg/dscm, which is similar to that obtained in the purged train. This result is expected since the purge is meant to only affect the inorganic CPM catch. The relative proportions of the CPM constituents are fairly consistent between the two trains, however. Ninety-two percent of the inorganic CPM is accounted for by the sulfate, with an average concentration of 4.7

mg/dscm. Eighty-five percent of the CPM is found in the inorganic fraction and 13 percent in the organic fraction (the remaining mass is accounted for by the back-half filter and is not characterized).

Additionally, the resuspended inorganic residues of the two trains were analyzed for a broader range of elements and ions in order to more fully speciate the inorganic CPM. These results are presented in Table 4-8. Sulfate, ammonium, sodium and calcium are the four most abundant compounds in the inorganic CPM fraction for both trains.

Purged Train. $\text{SO}_4^{=}$, NH_4^{+} , Na and Ca account for an average of 18.7 mg/dscm, or 107 percent, of the inorganic CPM mass as presented in Table 4-8. The remaining 29 elements and ions that were detected account for an average of 0.2 mg/dscm, or 1 percent, of the average inorganic CPM mass.

Unpurged Train. $\text{SO}_4^{=}$, NH_4^{+} , Na and Ca account for an average of 6.4 mg/dscm, which is approximately 125 percent of the inorganic CPM mass as presented in Table 4-8. The remaining constituents account for an additional 4 percent.

Although the results do not match expected behavior, the additional analysis confirms that $\text{SO}_4^{=}$ is the dominant compound in the inorganic residue. Ammonium is also present in significant amounts. It is believed the majority of $\text{SO}_4^{=}$, found in the impinger contents is an artifact resulting from gaseous SO_2 in the stack gas. These results and issues are discussed in more detail in Section 7.

Table 4-8. Speciation (mg/dscm) of Back-Half Impinger Catch (Site 1).

	Run 1 (mg/dscm)		Run 2 (mg/dscm)		Run 3 (mg/dscm)		Run 4 (mg/dscm)		Average (mg/dscm)	
	Purged	Unpurged	Purged	Unpurged	Purged	Unpurged	Purged	Unpurged	Purged	Unpurged
Sulfate	1.87E+1	5.78E+0	1.07E+1	2.96E+0	1.06E+1	5.76E+0	1.52E+1	4.38E+0	1.4E+01	4.7E+00
Ammonium	6.15E+0	1.71E+0	3.57E+0	3.80E-1	3.30E+0	1.64E+0	4.84E+0	1.18E+0	4.5E+00	1.2E+00
Na	3.08E-1	3.37E-1	2.38E-1	2.32E-1	2.83E-1	3.33E-1	3.14E-1	3.50E-1	2.9E-01	3.1E-01
Ca	1.43E-1	1.35E-1	6.19E-2	7.82E-2	1.15E-1	1.09E-1	8.47E-2	1.34E-1	1.0E-01	1.1E-01
Fe	1.65E-2	5.06E-2	6.90E-2	7.18E-3	9.42E-2	2.44E-1	1.43E-1	1.42E-2	8.1E-02	7.9E-02
K	< 3.08E-2	3.37E-2	3.10E-2	2.96E-2	< 2.59E-2	2.66E-2	3.87E-2	< 2.41E-2	< 3.2E-02	2.9E-02
Al	1.79E-2	2.12E-2	1.69E-2	1.10E-2	2.83E-2	3.55E-2	2.66E-2	1.03E-2	2.2E-02	1.9E-02
Mg	1.93E-2	2.65E-2	8.81E-3	9.51E-3	2.05E-2	1.49E-2	1.26E-2	1.45E-2	1.5E-02	1.6E-02
Ni	1.82E-3	9.88E-3	1.12E-2	< 4.65E-4	1.48E-2	6.43E-2	2.66E-2	1.20E-3	1.4E-02	< 1.9E-02
Cr	3.08E-4	2.65E-3	9.76E-3	2.75E-4	1.15E-2	2.88E-2	2.66E-2	1.69E-3	1.2E-02	8.4E-03
Si	< 3.08E-3	5.54E-3	7.38E-3	< 2.32E-3	9.90E-3	4.66E-3	2.37E-2	4.82E-3	< 1.1E-02	< 4.3E-03
Fluoride	< 6.99E-3	6.03E-3	6.67E-3	7.82E-3	9.66E-3	1.35E-2	< 6.05E-3	3.07E-3	< 7.3E-03	7.6E-03
Z	1.04E-2	8.92E-3	6.67E-3	1.31E-3	6.60E-3	6.65E-3	4.11E-3	3.07E-3	6.9E-03	5.0E-03
Chloride	< 6.99E-3	1.61E-2	< 5.95E-3	6.13E-3	< 5.89E-3	ND	< 6.05E-3	ND	< 6.2E-03	< 1.1E-02
Mn	6.43E-3	1.40E-1	5.48E-3	4.01E-4	8.01E-3	6.21E-2	1.91E-3	7.88E-4	5.5E-03	5.1E-02
B	3.36E-3	3.37E-3	5.24E-3	3.17E-4	8.01E-3	4.88E-3	4.84E-3	9.42E-4	5.4E-03	2.4E-03
Nitrate (as N)	4.48E-3	3.86E-3	ND	3.38E-3	3.53E-3	3.55E-3	3.87E-3	3.29E-3	< 4.0E-03	3.5E-03
Cu	4.48E-3	4.34E-3	9.05E-4	4.01E-4	1.70E-3	1.53E-2	1.69E-3	7.23E-4	2.2E-03	5.2E-03
Mo	< 1.54E-4	2.39E-4	1.12E-3	< 1.16E-4	1.25E-3	1.80E-3	4.11E-3	3.50E-4	< 1.7E-03	< 6.3E-04
P	< 1.85E-3	5.06E-3	< 1.57E-3	< 1.39E-3	< 1.55E-3	1.46E-3	< 1.60E-3	< 1.45E-3	< 1.6E-03	< 2.3E-03
Tl	< 1.85E-3	< 1.59E-3	< 1.57E-3	< 1.39E-3	< 1.55E-3	< 1.46E-3	< 1.60E-3	< 1.45E-3	< 1.6E-03	< 1.5E-03
Sn	< 1.54E-3	< 1.33E-3	< 1.31E-3	< 1.16E-3	< 1.30E-3	< 1.22E-3	< 1.33E-3	< 1.20E-3	< 1.4E-03	< 1.2E-03
Pb	< 6.15E-4	< 5.30E-4	< 5.24E-4	6.55E-4	< 5.18E-4	< 4.88E-4	< 5.32E-4	< 4.82E-4	< 5.5E-04	< 5.4E-04
Sr	4.76E-4	1.18E-3	3.33E-4	3.38E-4	6.13E-4	8.20E-4	6.05E-4	7.45E-4	5.1E-04	7.7E-04
Co	< 3.08E-4	2.41E-3	2.62E-4	< 2.32E-4	3.06E-4	1.37E-3	5.08E-4	< 2.41E-4	< 3.5E-04	< 1.1E-03
Ti	< 3.08E-4	< 2.65E-4	< 2.62E-4	< 2.32E-4	< 2.59E-4	3.55E-4	3.87E-4	3.29E-4	< 3.0E-04	< 3.0E-04
Ag	< 3.08E-4	7.71E-4	< 2.62E-4	< 2.32E-4	< 2.59E-4	5.10E-4	< 2.66E-4	< 2.41E-4	< 2.7E-04	< 4.4E-04
V	< 3.08E-4	< 2.65E-4	< 2.62E-4	< 2.32E-4	< 2.59E-4	< 2.44E-4	< 2.66E-4	< 2.41E-4	< 2.7E-04	< 2.5E-04
Zr	< 3.08E-4	< 2.65E-4	< 2.62E-4	< 2.32E-4	< 2.59E-4	< 2.44E-4	< 2.66E-4	< 2.41E-4	< 2.7E-04	< 2.5E-04
Cd	8.11E-4	2.05E-4	5.71E-5	< 4.65E-5	7.54E-5	1.22E-3	< 5.32E-5	9.64E-5	2.5E-04	< 3.9E-04
Ba	1.40E-4	1.11E-3	1.50E-4	2.75E-4	1.48E-4	3.10E-4	1.69E-4	3.07E-4	1.5E-04	5.0E-04
Be	< 3.08E-5	< 2.65E-5	< 2.62E-5	< 2.32E-5	< 2.59E-5	< 2.44E-5	< 2.66E-5	< 2.41E-5	< 2.7E-05	< 2.5E-05

< - one or two runs is below limit of quantitation (Detection limit x 3.33)

n/a-not applicable; two or more runs not detected

ND-not detected

4.1.5 Dilution Tunnel Results

Particulate Mass

PM2.5 mass measurements using the dilution tunnel include both solid aerosols that are directly emitted and those that condense under simulated stack plume conditions in the residence chamber. The dilution tunnel determines only the PM2.5 fraction of particulate emissions. Results from these measurements show that PM2.5 concentrations and emission rates average 0.03 mg/dscm and 0.0061 lb/hr, respectively, with a relative standard deviation of 11 percent, based on Teflon filter weight (Table 4-9). These results are almost three orders of magnitude lower than the sum of FPM2.5 and CPM measured by EPA Methods PRE-4 and 202. PM2.5 concentration measured in the process heater stack gas was approximately equal to the concentration measured in the ambient air.

Table 4-9. Dilution Tunnel PM2.5 Results (Site 1).

	Units	Results						
Run Number	-	1	2	3	4	Average	RSD	Ambient
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
PM2.5	mg/dscm	2.9E-2	3.2E-2	ND	2.6E-2	2.9E-2	11%	3.0E-2
	lb/hr	6.3E-3	6.9E-3	ND	5.1E-3	6.1E-3	15%	n/a

n/a-not applicable

RSD- Relative standard deviation

The concentration of PM2.5 using the dilution tunnel is an order of magnitude lower than FPM <2.5 micrometers measured using Method PRE-4 and almost three orders of magnitude lower than CPM measured using Method 202. CPM is normally included in regulatory definitions of PM10. These emission measurements are strongly method dependent because the dilution tunnel replicates conditions experienced by the stack emissions as they mix with the atmosphere more accurately than Method 202. Due to suspected artifacts associated with Method 202, it is believed the dilution tunnel results are more representative of the true primary PM2.5 emissions.

Sulfate, Chloride, and Nitrate

Quartz filters were analyzed for SO_4^- , Cl^- , NO_3^- and NH_4^+ ion. Of these, SO_4^- had the highest average concentration at 0.02 mg/dscm, followed by NH_4^+ at 0.009 mg/dscm (Table 4-10). All

ions in the field blank were present below detectable levels (see Section 6 for additional discussion of blanks).

Table 4-10. Dilution Tunnel Sulfate, Nitrate, and Chloride Results (Site 1).

Parameter	Units	Value						
Run Number	-	1	2	3	4	Average	RSD	Ambient
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
Sulfate	mg/dscm	1.4E-2	2.3E-2	9.2E-3	3.3E-2	2.0E-2	53%	1.3E-3
	lb/hr	3.0E-3	4.8E-3	2.0E-3	6.5E-3	4.1E-3	49%	n/a
Nitrate	mg/dscm	4.6E-3	7.5E-3	3.5E-3	3.1E-3	4.7E-3	43%	5.6E-4
	lb/hr	9.9E-4	1.6E-3	7.4E-4	6.1E-4	9.8E-4	45%	n/a
Chloride	mg/dscm	ND	ND	1.6E-3	1.8E-3	1.7E-3	10%	1.9E-3
	lb/hr	ND	ND	3.3E-4	3.5E-4	3.4E-4	4%	n/a
Ammonium	mg/dscm	ND	1.0E-2	4.2E-3	1.3E-2	9.0E-3	49%	2.9E-4
	lb/hr	ND	2.1E-3	8.9E-4	2.5E-3	1.8E-3	46%	n/a

n/a - not applicable

ND - not detected

RSD- Relative standard deviation

The quartz filters used for these measurements have the potential for a positive $\text{SO}_4^{=}$ bias. The average $\text{SO}_4^{=}$ concentration from the dilution tunnel is approximately 3 orders of magnitude lower than the average concentration reported above for Method 202. This difference lends further support to the possibility of a significant sampling artifact in Method 202 due to gaseous SO_2 in the stack gas. Concentrations of nitrate measured in the stack gas are within an order of magnitude of the concentrations measured in the ambient air. Chloride was detected in the ambient sample at levels approximately equal to those in the field samples.

OC, EC and Organic Species

OC and EC were measured on quartz filters from the dilution tunnel. OC concentration ranged from 0.046 to 0.062 mg/dscm. EC was detected at concentrations of 0.0026 and 0.0094 mg/dscm (Table 4-11). OC accounts for approximately 96 percent of the total carbon mass. Average elemental carbon concentrations measured in the stack gas are within an order of magnitude of the ambient sample concentration; the average OC concentration is slightly more than an order of magnitude greater than the ambient concentration. Organic and elemental carbon were below detection limits in the field blank (see Section 6 for additional discussion of blank results).

Table 4-11. OC/EC as Measured by the Dilution Tunnel (Site 1).

Parameter	Units	Value						
Run Number	-	1	2	3	4	Average	RSD	Ambient
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
Organic Carbon	mg/dscm	0.06	0.05	0.05	0.05	0.05	15%	3.5E-3
	lb/hr	0.013	0.010	0.010	0.009	0.011	18%	n/a
Elemental Carbon	mg/dscm	5.9E-3	4.6E-3	2.6E-3	9.4E-3	5.6E-3	52%	7.8E-4
	lb/hr	1.3E-3	9.8E-4	5.4E-4	1.8E-3	1.2E-3	47%	n/a
Total Carbon	mg/dscm	0.07	0.05	0.05	0.05	0.05	20%	4.3E-3
	lb/hr	1.5E-2	9.8E-3	9.7E-3	9.5E-3	1.1E-2	22%	n/a

SVOCs were determined on the combined TIGF/PUF/XAD-4/PUF cartridge used with the dilution tunnel. This method determines both particulate and vapor phase SVOCs together. Results of the stack emissions and ambient air sample are presented in Table 4-12. Naphthalene is the most abundant SVOC in the dilution tunnel samples with an average concentration of 0.0034 mg/dscm. All of the average SVOC stack gas concentrations are a factor of ten greater than the ambient air concentration, with the minimum being a factor of 14.

Tenax. Tenax sorbent was used to collect VOCs. The analysis of Tenax focused only on VOCs with a carbon number greater than seven since these are believed to be the most significant precursors for secondary organic aerosols. Tubes for Runs 2 and 4 were damaged during sampling and could not be analyzed. Benzaldehyde was the most abundant VOC detected during sampling, with an average concentration of 0.16 mg/dscm (Table 4-13). Hexadecanoic acid was the second most abundant on average (0.14 mg/dscm). In general, the average VOC concentration in the stack gas was within a factor of approximately ten to forty times the ambient air concentration. Concentrations of 1,2,4-trimethylbenzene, 4-ethyl-o-xylene, 5-ethyl-m-xylene, decanal, and p-ethyltoluene were all lower in the field samples than in the ambient sample.

Canisters. Stainless steel canisters were used to collect VOCs and the analysis of the sample obtained from the canisters allows for detection of organic species with carbon numbers as low as two. Results from the canister samples are presented in Table 4-14. Propene and n-butane were the two highest detected compounds with concentrations of 4.4 mg/dscm and 3.4 mg/dscm respectively. All concentrations at detectable levels in the stack samples are at least five times larger than concentrations in the ambient sample, with most being an order of magnitude larger.

Table 4-12. Semi-Volatile Organic Compound (SVOC) Results (mg/dscm) (Site 1).

Parameter	Value							
Run Number	1	2	3	4	Average	RSD	Ambient	MDL
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		(%)	22-Feb-01	
Naphthalene	3.4E-3	ND	ND	ND	3.4E-3	n/a	ND	5.1E-5
2-methylnaphthalene	6.5E-3	1.9E-3	1.9E-3	1.4E-3	2.9E-3	83	7.7E-5	3.3E-6
1-methylnaphthalene	2.9E-3	8.5E-4	9.0E-4	6.4E-4	1.3E-3	80	3.7E-5	2.0E-6
1,3+1,6+1,7-dimethylnaphthalene	1.5E-3	5.1E-4	7.3E-4	4.3E-4	8.0E-4	62	1.8E-5	1.2E-5
2-ethyl-1-methylnaphthalene	9.1E-4	4.7E-4	ND	3.6E-4	5.8E-4	50	1.6E-5	8.8E-6
2,6+2,7-dimethylnaphthalene	9.3E-4	3.3E-4	4.1E-4	2.6E-4	4.8E-4	63	1.1E-5	5.7E-6
1+2-ethylnaphthalene	5.5E-4	2.1E-4	2.6E-4	1.8E-4	3.0E-4	56	7.6E-6	6.8E-6
Benz(a)anthracene	8.0E-5	8.9E-4	9.6E-5	6.3E-5	2.8E-4	143	1.2E-5	3.2E-7
1,4+1,5+2,3-dimethylnaphthalene	3.2E-4	ND	1.7E-4	ND	2.5E-4	44	ND	5.4E-6
9-fluorenone	1.8E-4	ND	1.8E-4	2.4E-4	2.0E-4	15	ND	7.1E-6
Acenaphthylene	2.0E-4	ND	1.7E-4	ND	1.8E-4	10	ND	5.5E-6
A-trimethylnaphthalene	2.9E-4	1.0E-4	1.3E-4	8.6E-5	1.5E-4	61	5.6E-6	1.0E-7
Biphenyl	1.5E-4	ND	ND	ND	1.5E-4	n/a	ND	3.6E-6
C-dimethylphenanthrene	1.3E-4	ND	1.7E-4	1.1E-4	1.4E-4	24	8.9E-6	1.8E-6
C-trimethylnaphthalene	2.0E-4	7.9E-5	1.3E-4	1.1E-4	1.3E-4	41	4.4E-6	4.2E-7
B-trimethylnaphthalene	2.1E-4	7.9E-5	1.1E-4	7.7E-5	1.2E-4	52	4.1E-6	5.3E-8
2,3,5-I-trimethylnaphthalene	1.4E-4	5.9E-5	8.9E-5	3.5E-5	8.2E-5	57	3.2E-6	1.6E-7
Phenanthrene	1.1E-4	3.9E-5	1.3E-4	4.4E-5	7.8E-5	56	4.0E-6	4.2E-7
E-dimethylphenanthrene	7.3E-5	ND	ND	ND	7.3E-5	n/a	ND	8.0E-7
7-methylbenz(a)anthracene	3.3E-5	1.5E-4	ND	2.2E-5	6.8E-5	104	4.4E-6	3.3E-7
1-ethyl-2-methylnaphthalene	8.6E-5	3.9E-5	5.3E-5	4.4E-5	5.6E-5	38	1.7E-6	1.1E-7
J-trimethylnaphthalene	3.8E-5	5.2E-5	7.2E-5	5.3E-5	5.4E-5	26	1.8E-6	4.3E-7
E-trimethylnaphthalene	8.1E-5	3.5E-5	6.4E-5	3.3E-5	5.3E-5	44	1.8E-6	5.3E-8
D-dimethylphenanthrene	5.2E-5	ND	ND	ND	5.2E-5	n/a	ND	1.6E-6
Benzo(e)pyrene	ND	ND	ND	3.4E-5	3.4E-5	n/a	ND	3.3E-7
C-MePy/MeFl	6.5E-6	3.0E-6	9.4E-5	1.7E-5	3.0E-5	142	1.7E-6	5.3E-8
Fluoranthene	1.6E-5	1.8E-5	2.7E-5	1.3E-5	1.9E-5	33	8.6E-7	1.1E-7
2-methylphenanthrene	2.2E-5	1.6E-5	1.9E-5	7.2E-6	1.6E-5	41	3.7E-7	1.1E-7
Benzanthrone	1.5E-5	ND	ND	ND	1.5E-5	n/a	8.1E-7	4.8E-7
Chrysene	1.7E-5	ND	9.7E-6	1.1E-5	1.3E-5	29	3.2E-7	1.1E-7
Benzo(a)pyrene	1.2E-5	ND	ND	ND	1.2E-5	n/a	4.4E-7	3.2E-7
Pyrene	1.1E-5	ND	1.3E-5	ND	1.2E-5	11	3.9E-7	2.1E-7
D-MePy/MeFl	3.6E-6	4.9E-6	2.9E-5	9.0E-6	1.2E-5	102	7.9E-7	5.3E-8
2,4,5-trimethylnaphthalene	1.2E-5	ND	ND	ND	1.2E-5	n/a	ND	4.2E-7
B-MePy/MeFl	ND	6.1E-6	ND	ND	6.1E-6	n/a	1.7E-7	5.3E-8
5+6-methylchrysene	7.2E-6	4.2E-6	5.5E-6	7.2E-6	6.0E-6	24	ND	0.0E+0
Anthrone	8.7E-6	1.8E-6	2.4E-6	ND	4.3E-6	88	7.4E-8	5.3E-8
Benzonaphthothiophene	2.9E-6	ND	ND	ND	2.9E-6	n/a	1.5E-7	1.1E-7
Anthracene	ND	ND	1.8E-6	ND	1.8E-6	n/a	ND	0.0E+0
1,4,5-trimethylnaphthalene	ND	ND	ND	ND	ND	n/a	5.4E-6	5.0E-6
Dibenzofuran	ND	ND	ND	ND	ND	n/a	4.2E-6	3.3E-6
7-methylbenzo(a)pyrene	ND	ND	ND	ND	ND	n/a	1.6E-6	3.7E-7
Benzo(c)phenanthrene	ND	ND	ND	ND	ND	n/a	8.1E-7	5.8E-7
Xanthone	ND	ND	ND	ND	ND	n/a	7.6E-7	2.1E-7

n/a- not applicable; only one run within detectable limits.

ND- Not detected

MDL- Method detection limit

RSD- Relative standard deviation

Table 4-13. Volatile Organic Compound (VOC) Results from Tenax (Site 1).

Parameter	Value						
Units	mg/dscm					%	mg/dscm
Run Number	1	2	3	4	Average	RSD	Ambient
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
Benzaldehyde	2.2E-1		1.0E-1		1.6E-1	49	3.9E-3
Hexadecanoic acid	2.3E-1		5.3E-2		1.4E-1	89	1.1E-2
Styrene	1.2E-1		1.8E-2		6.9E-2	105	7.5E-4
Acetophenone	8.2E-2		3.6E-2		5.9E-2	54	2.1E-3
Phenol	4.0E-2		1.6E-2		2.8E-2	61	8.2E-4
Nonanal	2.4E-2		6.2E-3		1.5E-2	84	3.3E-4
m&p-xylene	1.0E-2		9.0E-3		9.7E-3	9	9.0E-4
Nonane	6.8E-3		4.4E-3		5.6E-3	31	2.8E-4
Decanal	ND		1.1E-2		5.3E-3	n/a	6.7E-4
m/p-methylphenol	4.7E-3		ND		4.7E-3	n/a	6.4E-5
Ethylbenzene	6.0E-3		3.1E-3		4.6E-3	44	2.8E-4
Decane	5.5E-3		2.4E-3		3.9E-3	55	2.1E-4
Heptanal	3.7E-3		ND		3.7E-3	n/a	ND
Biphenyl	5.1E-3		2.3E-3		3.7E-3	55	1.0E-4
Undecane	4.5E-3		2.5E-3		3.5E-3	41	2.6E-4
o-xylene	3.9E-3		3.0E-3		3.5E-3	18	3.1E-4
Dodecene	2.1E-3		3.7E-3		2.9E-3	37	1.7E-4
Dodecane	3.1E-3		1.7E-3		2.4E-3	40	1.9E-4
1,2,4-trimethylbenzene	1.9E-3		2.8E-3		2.4E-3	26	2.7E-4
m-ethyltoluene	2.6E-3		2.1E-3		2.4E-3	17	1.9E-4
1-undecene	3.4E-3		1.3E-3		2.3E-3	62	7.8E-5
Naphthalene	2.9E-3		1.4E-3		2.2E-3	48	8.4E-5
1-nonene	2.2E-3		1.5E-3		1.9E-3	26	9.6E-5
2,3-benzofuran	2.8E-3		9.2E-4		1.8E-3	71	5.5E-5
Pentadecane	1.4E-3		ND		1.4E-3	n/a	ND
1,3-dichlorobenzene	1.5E-3		1.3E-3		1.4E-3	9	7.3E-5
4-methylstyrene	2.0E-3		6.0E-4		1.3E-3	77	ND
C-dimethylindane	1.4E-3		1.1E-3		1.3E-3	18	9.2E-5
2-heptanone	1.2E-3		ND		1.2E-3	n/a	ND
Propylbenzene	1.6E-3		6.9E-4		1.1E-3	55	5.9E-5
Tetradecane	1.1E-3		9.2E-4		1.0E-3	16	5.1E-5
4-tert-butyltoluene	9.0E-4		ND		9.0E-4	n/a	ND
o-ethyltoluene	1.0E-3		7.2E-4		8.6E-4	23	8.1E-5
p-ethyltoluene	6.6E-4		9.7E-4		8.1E-4	27	1.2E-4
Indene	8.1E-4		ND		8.1E-4	n/a	ND
(+/-)-limonene	6.6E-4		6.9E-4		6.8E-4	4	ND
1,3,5-trimethylbenzene	4.1E-4		8.4E-4		6.3E-4	48	6.1E-5
Tridecane	5.6E-4		6.0E-4		5.8E-4	4	4.6E-5
2-methylnaphthalene	7.3E-4		4.2E-4		5.8E-4	38	4.5E-5
1,2-diethylbenzene	4.9E-4		3.7E-4		4.3E-4	19	ND
Hexadecane	3.9E-4		ND		3.9E-4	n/a	ND
1-methylnaphthalene	4.1E-4		2.7E-4		3.4E-4	29	ND
Phenanthrene	ND		6.0E-4		3.0E-4	n/a	ND
4-ethyl-o-xylene	4.1E-4		1.5E-4		2.8E-4	67	3.6E-5
Heptadecane	2.2E-4		ND		2.2E-4	n/a	ND
5-ethyl-m-xylene	ND		4.2E-4		2.1E-4	n/a	5.3E-5
1,2,4,5-tetramethylbenzene	9.8E-5		ND		9.8E-5	n/a	ND
1,3-diethylbenzene	ND		1.5E-4		7.4E-5	n/a	ND
2-ethyl-p-xylene	ND		1.5E-4		7.4E-5	n/a	ND
1,2,3,4-tetramethylbenzene	ND		1.5E-4		7.4E-5	n/a	ND
1,2-dichlorobenzene	ND		1.2E-4		6.2E-5	n/a	ND
4-n-propyltoluene + 1,4-diethylbenzene	4.9E-5		ND		4.9E-5	n/a	ND
2-n-propyltoluene	ND		7.4E-5		3.7E-5	n/a	ND
Cyclohexanone	ND		ND		ND	n/a	2.7E-4
1-decene	ND		ND		ND	n/a	2.0E-4
1-methylindan	ND		ND		ND	n/a	6.8E-5
3-methyloctane	ND		ND		ND	n/a	5.1E-5
Indan	ND		ND		ND	n/a	3.3E-5
Propylcyclohexane	ND		ND		ND	n/a	3.2E-5

n/a-not applicable. Less than two runs within detectable limits.

RSD-relative standard deviation.

ND-not detected.

Table 4-14. Volatile Organic Compound (VOC) Results from Canisters (Site 1).

Parameter	Value						
Units	mg/dscm					%	mg/dscm
Run Number	1	2	3	4	Average	RSD	Ambient
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
1,1-dimethylcyclohexane	ND	5.66E-3	ND	1.35E-2	9.56E-3	58	3.67E-4
1,2,3,4-tetramethylbenzene	1.20E-2	1.08E-2	6.80E-3	1.74E-2	1.18E-2	37	7.14E-4
1,2,3,5-tetramethylbenzene	1.20E-2	1.90E-2	3.13E-2	2.28E-2	2.13E-2	38	3.84E-4
1,2,3-trimethylbenzene	4.80E-3	2.67E-2	4.88E-3	2.40E-3	9.69E-3	118	2.46E-4
1,2,4,5-tetramethylbenzene	9.37E-3	1.08E-2	1.77E-2	5.36E-3	1.08E-2	47	2.74E-4
1,2,4-trimethylbenzene	2.52E-2	3.64E-2	4.63E-2	2.88E-2	3.42E-2	27	2.61E-3
1,2-diethylbenzene	2.28E-2	2.57E-2	6.80E-3	8.05E-3	1.58E-2	62	1.04E-3
1,3,5-trimethylbenzene	7.19E-3	1.70E-2	1.83E-2	1.32E-2	1.39E-2	36	1.57E-3
1,3-butadiene	1.08E-3	4.37E-3	8.23E-3	7.57E-3	5.31E-3	62	5.09E-4
1,3-diethylbenzene	5.62E-2	8.53E-2	8.03E-2	1.21E-2	5.85E-2	57	9.88E-4
1,3-dimethylcyclopentane	8.82E-3	2.68E-2	1.59E-2	1.08E-2	1.56E-2	52	1.00E-3
1,4-diethylbenzene	2.14E-2	1.90E-2	2.72E-2	1.88E-2	2.16E-2	18	1.98E-3
1-butene	4.98E-2	1.79E-1	3.21E-1	2.53E-1	2.01E-1	58	2.23E-3
1-hexene	ND	5.52E-2	7.77E-2	3.36E-3	4.54E-2	84	1.34E-3
1-methylcyclopentene	8.19E-4	7.46E-3	5.83E-3	2.46E-3	4.14E-3	73	1.34E-4
1-methylindan	9.23E-3	6.67E-3	4.02E-3	ND	6.64E-3	39	1.08E-4
1-pentene	7.00E-3	8.56E-2	9.24E-2	5.89E-2	6.10E-2	64	2.70E-3
2,2,4-trimethylpentane	2.39E-2	5.88E-2	4.52E-2	2.28E-2	3.77E-2	46	5.28E-3
2,2,5-trimethylhexane	ND	4.53E-2	ND	ND	4.53E-2	n/a	ND
2,2-dimethylbutane	5.16E-3	2.52E-2	1.75E-2	8.61E-3	1.41E-2	64	9.52E-4
2,3,4-trimethylpentane	7.98E-3	2.07E-2	1.39E-2	1.48E-2	1.44E-2	36	2.15E-3
2,3,5-trimethylhexane*	4.17E-1	5.75E-1	1.95E+0	8.60E-1	9.50E-1	73	2.62E-2
2,3-dimethylbutane	1.12E-2	4.61E-2	2.62E-2	1.72E-2	2.52E-2	61	1.97E-3
2,3-dimethylhexane	9.12E-3	ND	3.47E-3	ND	6.30E-3	63	ND
2,3-dimethylpentane	1.20E-2	3.13E-2	2.03E-2	1.10E-2	1.87E-2	50	3.03E-3
2,4,4-trimethyl-1-pentene	1.01E-2	1.13E-2	2.28E-2	4.48E-3	1.22E-2	63	3.21E-4
2,4-dimethylhexane	1.14E-3	1.15E-3	1.16E-3	1.14E-3	1.15E-3	1	1.40E-4
2,4-dimethylheptane	ND	ND	ND	ND	ND	n/a	1.05E-4
2,4-dimethylpentane	8.00E-3	2.53E-2	1.83E-2	1.20E-2	1.59E-2	48	1.56E-3
2,5-dimethylhexane	5.70E-3	8.07E-3	1.27E-2	4.57E-3	7.77E-3	47	6.07E-4
2,5-dimethylheptane	5.12E-3	1.04E-2	9.10E-3	3.84E-3	7.11E-3	44	5.25E-4
2,6-dimethylheptane	5.12E-3	6.47E-3	3.90E-3	3.84E-3	4.83E-3	26	3.15E-4
2,6-dimethyloctane	1.85E-2	1.87E-2	1.73E-2	3.98E-2	2.36E-2	46	6.98E-4
2-methyl-1-butene	7.00E-3	4.03E-2	2.92E-2	1.54E-2	2.30E-2	64	3.13E-3
2-methyl-1-pentene	8.39E-4	5.94E-3	3.41E-3	2.52E-3	3.18E-3	67	1.38E-4
2-methyl-2-butene	1.19E-2	5.31E-2	7.11E-3	1.75E-2	2.24E-2	93	8.03E-4
2-methyl-2-pentene	ND	7.64E-3	5.12E-3	5.05E-3	5.94E-3	25	2.41E-4
2-methylheptane	8.96E-3	2.20E-2	1.43E-2	1.15E-2	1.42E-2	40	1.52E-3
2-methylhexane	1.18E-2	3.77E-2	3.09E-2	1.77E-2	2.45E-2	48	2.41E-3
2-methylpentane	3.70E-2	1.37E-1	7.95E-2	4.65E-2	7.49E-2	60	5.46E-3
2-methylpropanal	ND	ND	ND	ND	ND	n/a	8.84E-5
3,3-dimethylheptane	1.28E-3	6.47E-3	2.60E-3	2.56E-3	3.23E-3	70	2.62E-4
3,3-dimethylpentane	3.00E-3	4.04E-3	6.10E-3	2.00E-3	3.79E-3	46	2.46E-4
3,6-dimethyloctane	1.99E-2	2.15E-2	4.33E-2	3.13E-2	2.90E-2	37	9.31E-4
3-ethylpentane	4.56E-3	2.88E-2	2.08E-2	1.03E-2	1.61E-2	67	1.31E-3
3-methyl-1-butene	2.80E-3	2.19E-2	2.06E-2	1.19E-2	1.43E-2	62	2.01E-4
3-methyl-2-pentene	ND	6.79E-3	3.41E-3	3.36E-3	4.52E-3	43	2.41E-4
3-methylheptane	5.70E-3	1.27E-2	1.27E-2	7.99E-3	9.78E-3	36	1.12E-3
3-methylhexane + pentanal	1.50E-2	4.55E-2	4.67E-2	3.00E-2	3.43E-2	44	3.07E-3
3-methyloctane	1.02E-2	5.18E-3	9.10E-3	7.69E-3	8.05E-3	27	1.57E-4
3-methylpentane	2.23E-2	1.43E-1	6.55E-2	3.01E-2	6.54E-2	85	3.49E-3
4,4-dimethylheptane	3.84E-3	5.18E-3	3.90E-3	5.13E-3	4.51E-3	16	4.72E-4
4-methylheptane	1.28E-3	7.77E-3	2.60E-3	6.41E-3	4.51E-3	68	5.77E-4
4-methylhexene	9.79E-4	1.98E-3	3.98E-3	9.81E-4	1.98E-3	71	1.20E-4

Table 4-14. Volatile Organic Compound (VOC) Results from Canisters (Site 1) (Continued).

Parameter	Value						
Units	mg/dscm					%	mg/dscm
Run Number	1	2	3	4	Average	RSD	Ambient
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
acetone	1.62E-2	ND	1.39E-1	1.80E-1	1.12E-1	76	1.95E-3
acetylene	1.17E-1	2.30E-1	1.37E-1	7.57E-2	1.40E-1	47	1.95E-3
benzaldehyde	ND	2.14E-3	2.15E-3	1.06E-3	1.78E-3	35	3.47E-4
benzene	3.97E-2	7.09E-2	1.04E-1	1.29E-1	8.58E-2	45	3.96E-3
beta-pinene	2.45E-2	8.25E-3	1.38E-2	1.36E-2	1.50E-2	45	5.57E-4
C10 aromatic 1	4.02E-3	6.77E-3	5.44E-3	4.02E-3	5.06E-3	26	2.20E-4
C10 aromatic 2	9.37E-3	6.77E-3	5.44E-3	6.71E-3	7.07E-3	23	6.04E-4
C10 aromatic 4	2.68E-3	2.71E-3	4.08E-3	1.34E-3	2.70E-3	41	2.20E-4
C10 aromatic 5	8.03E-3	1.22E-2	1.36E-2	6.71E-3	1.01E-2	32	3.84E-4
C10 aromatic 6	6.69E-3	1.35E-2	4.08E-3	ND	8.11E-3	60	ND
C10 olefin 2	3.92E-2	6.09E-2	5.26E-2	3.22E-2	4.62E-2	28	ND
C10 paraffin a	3.12E-2	4.88E-2	5.92E-2	7.11E-3	3.66E-2	62	7.57E-4
C10 paraffin c	3.97E-2	5.31E-2	5.34E-2	7.11E-3	3.83E-2	57	3.49E-4
C11 aromatic 1	2.96E-3	7.48E-3	7.51E-3	ND	5.98E-3	44	1.82E-4
C11 aromatic 3	ND	ND	ND	ND	ND	n/a	1.82E-4
C11 paraffin a	4.68E-3	4.73E-3	ND	ND	4.71E-3	1	2.56E-4
c-2-butene	6.21E-2	1.76E-1	1.90E-1	1.49E-1	1.44E-1	40	7.57E-4
c-2-hexene	ND	5.94E-3	5.12E-3	ND	5.53E-3	11	ND
c-2-pentene	4.20E-3	2.26E-2	1.78E-2	1.12E-2	1.40E-2	57	3.73E-4
c-3-hexene	ND	8.49E-3	4.27E-3	1.68E-3	4.81E-3	71	1.03E-4
c-3-hexene	5.88E-3	5.10E-3	5.12E-3	5.05E-3	5.28E-3	7	6.88E-5
C6 olefin 1	2.52E-3	3.40E-3	2.56E-3	3.36E-3	2.96E-3	16	6.88E-5
C7 olefin 1	ND	4.95E-3	1.99E-3	1.96E-3	2.97E-3	58	1.20E-4
C7 olefin 2	1.96E-3	1.98E-3	ND	ND	1.97E-3	1	4.02E-5
C8 olefin 1	2.24E-3	4.53E-3	5.69E-3	3.36E-3	3.96E-3	38	2.75E-4
C8 olefin 2	1.12E-3	ND	1.14E-3	ND	1.13E-3	1	4.59E-5
C8 olefin 3	1.57E-2	1.47E-2	6.83E-3	3.36E-3	1.01E-2	59	9.18E-5
C8 paraffin 1	ND	ND	ND	ND	ND	n/a	ND
C8 paraffin 2	4.56E-3	9.22E-3	9.27E-3	7.99E-3	7.76E-3	29	5.14E-4
C8 paraffin 3	ND	ND	ND	ND	ND	n/a	ND
C9 olefin 1	ND	ND	ND	ND	ND	n/a	ND
C9 olefin 2	3.78E-3	3.82E-3	7.68E-3	2.52E-3	4.45E-3	50	2.07E-4
C9 olefin 3	ND	5.10E-3	1.54E-2	5.05E-3	8.50E-3	70	4.65E-4
C9 olefin 4	3.78E-3	2.55E-3	5.12E-3	5.05E-3	4.12E-3	30	ND
C9 paraffin 1	2.56E-3	6.47E-3	6.50E-3	3.84E-3	4.84E-3	41	2.62E-4
C9 paraffin 2	2.56E-3	1.29E-3	1.30E-3	1.28E-3	1.61E-3	39	1.57E-4
C9 paraffin 3	2.56E-3	2.59E-3	3.90E-3	1.28E-3	2.58E-3	41	2.10E-4
chlorobenzene	1.12E-3	1.14E-3	1.14E-3	2.25E-3	1.41E-3	40	9.21E-5
cis-3-methyl-2-pentene	1.68E-3	4.25E-3	3.41E-3	2.52E-3	2.97E-3	37	1.38E-4
cyclohexane	2.51E-1	4.09E+0	1.90E+0	5.58E-1	1.70E+0	103	1.38E-3
cyclohexene	8.19E-4	3.32E-3	1.67E-3	8.21E-4	1.66E-3	71	1.34E-4
cyclopentane	1.33E-2	5.24E-2	4.55E-2	2.80E-2	3.48E-2	51	8.60E-4
cyclopentene	4.76E-3	1.31E-2	8.98E-3	4.76E-3	7.89E-3	50	8.36E-5
decene-1*	1.84E+0	1.34E+0	2.30E+0	1.62E+0	1.77E+0	23	3.13E-2
dodecene-1	3.40E-3	1.72E-3	ND	5.11E-3	3.41E-3	50	ND
ethane	5.92E-1	7.86E-1	4.41E-1	2.98E-1	5.29E-1	39	5.98E-3
ethanol	ND	1.39E-3	ND	ND	1.39E-3	n/a	ND
ethene	6.78E-1	1.95E-1	2.64E-1	9.30E-2	3.07E-1	83	1.58E-3
ethylbenzene	1.69E-2	2.57E-2	3.01E-2	1.91E-2	2.30E-2	26	2.30E-3
heptene-1	5.88E-3	1.59E-2	ND	ND	1.09E-2	65	ND
hexanal	4.30E-2	3.74E-2	8.73E-2	5.80E-2	5.64E-2	40	2.87E-3
indan	7.07E-3	7.15E-3	5.99E-3	5.90E-3	6.53E-3	10	6.28E-4
indene	4.63E-3	4.69E-3	5.89E-3	4.64E-3	4.96E-3	12	2.38E-4
isobutane	4.89E-1	1.68E+0	2.43E+0	2.22E+0	1.70E+0	51	ND
iso-butene	5.09E-2	1.83E-1	3.30E-1	2.61E-1	2.06E-1	58	2.75E-3

Table 4-14. Volatile Organic Compound (VOC) Results from Canisters (Site 1) (Continued).

Parameter	Value						
Units	mg/dscm					%	mg/dscm
Run Number	1	2	3	4	Average	RSD	Ambient
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
isobutylbenzene	4.15E-2	3.25E-2	2.59E-2	3.08E-2	3.27E-2	20	4.94E-4
isopentane	1.87E-1	1.02E+0	6.56E-1	3.50E-1	5.53E-1	66	1.35E-2
isoprene	ND	ND	ND	ND	ND	n/a	1.11E-4
isopropylbenzene	2.40E-3	3.64E-3	6.09E-3	1.20E-3	3.33E-3	63	3.93E-4
isopropylcyclohexane	3.78E-3	7.64E-3	7.68E-3	3.78E-3	5.72E-3	39	5.16E-4
isopropyltoluene	4.02E-3	8.13E-3	9.53E-3	8.05E-3	7.43E-3	32	1.65E-4
limonene	6.79E-3	2.75E-3	4.14E-3	4.08E-3	4.44E-3	38	5.01E-4
m- & p-xylene	5.61E-2	1.03E-1	1.16E-1	8.38E-2	8.98E-2	29	9.81E-3
methanol	9.27E-3	ND	7.60E-2	1.30E-1	7.19E-2	84	5.63E-4
methylcyclohexane	1.57E-2	4.26E-2	2.89E-2	3.14E-2	2.96E-2	37	2.25E-3
methylcyclopentane	6.04E-2	5.99E-1	2.10E-1	7.48E-2	2.36E-1	106	3.79E-3
m-ethyltoluene	2.04E-2	3.88E-2	3.66E-2	2.52E-2	3.02E-2	29	2.85E-3
MTBE	ND	5.34E-3	ND	ND	5.34E-3	n/a	1.08E-4
naphthalene	1.53E-2	1.68E-2	1.04E-2	1.66E-2	1.48E-2	20	5.77E-4
n-butane	1.74E+0	6.74E+0	2.97E+0	2.19E+0	3.41E+0	67	ND
n-decane	6.39E-2	5.17E-2	5.48E-2	2.99E-2	5.01E-2	29	2.04E-3
n-dodecane	6.80E-2	2.75E-2	3.28E-2	2.04E-2	3.72E-2	57	1.25E-3
n-heptane	1.90E-2	3.94E-2	3.96E-2	2.50E-2	3.08E-2	34	2.42E-3
n-hexane	1.74E-1	2.21E+0	3.93E-1	8.35E-2	7.15E-1	141	4.44E-3
n-nonane	1.28E-2	1.68E-2	2.08E-2	8.97E-3	1.48E-2	34	1.42E-3
n-octane	1.82E-2	1.96E-2	2.08E-2	1.71E-2	1.89E-2	9	1.26E-3
nonanal	ND	ND	ND	ND	ND	n/a	1.69E-2
nonene-1	ND	3.82E-3	1.28E-3	2.52E-3	2.54E-3	50	1.55E-4
n-pentane	5.76E-2	2.47E-1	1.54E-1	8.22E-2	1.35E-1	63	5.84E-3
n-propylbenzene	1.20E-2	1.58E-2	1.95E-2	1.20E-2	1.48E-2	24	1.03E-3
n-undecane	7.64E-2	5.20E-2	5.39E-2	3.12E-2	5.34E-2	35	2.88E-3
octanal	3.83E-3	7.75E-2	1.17E-1	1.21E-1	7.99E-2	68	7.59E-3
octene-1	6.72E-3	5.66E-3	5.69E-3	6.73E-3	6.20E-3	10	4.13E-4
o-ethyltoluene	8.39E-3	1.70E-2	1.83E-2	4.80E-3	1.21E-2	54	7.87E-4
o-xylene	2.65E-2	4.18E-2	4.84E-2	3.71E-2	3.85E-2	24	3.69E-3
p-ethyltoluene	1.03E-2	1.93E-2	2.68E-2	1.62E-2	1.81E-2	38	1.68E-3
propane	7.84E-1	2.59E+0	2.76E+0	1.69E+0	1.95E+0	47	1.61E-2
propene	6.30E-1	7.08E+0	5.56E+0	4.47E+0	4.43E+0	62	ND
sec-butylbenzene	2.68E-3	1.35E-3	ND	ND	2.02E-3	46	5.49E-5
styrene + heptanal	4.26E-2	5.04E-2	7.50E-2	7.39E-2	6.05E-2	27	3.71E-3
t-2-butene	2.74E-2	1.40E-1	2.17E-1	1.78E-1	1.41E-1	58	1.47E-3
t-2-hexene	2.52E-3	1.02E-2	6.83E-3	5.05E-3	6.15E-3	52	2.41E-4
t-2-pentene	7.00E-3	4.03E-2	3.48E-2	2.10E-2	2.58E-2	58	6.88E-4
t-3-heptene	ND	3.96E-3	4.98E-3	1.96E-3	3.63E-3	42	2.01E-4
toluene	3.78E-1	3.80E-1	4.60E-1	3.16E-1	3.83E-1	15	1.78E-2
Total Identified NMHC	2.30E+0	7.92E+0	6.13E+0	4.27E+0	5.15E+0	47	5.22E-2
Unidentified	1.82E-1	2.23E-1	2.94E-1	2.84E-1	2.46E-1	21	6.85E-3

n/a-not applicable. Less than two runs within detectable limits.

RSD-relative standard deviation.

ND-not detected.

* peak coelutes with chromatographic column bleed

Elements

Element concentrations were determined by XRF analysis of the TMFs used in the dilution tunnel. On average, S, Fe, Zn, Si, and Na are the most abundant elements in the stack gas (Table 4-15). The S results are within a factor of 3 of the dilution tunnel SO_4^- results presented earlier, as expected. Na and Mg results are considered semi-quantitative because of analytical limitations. Ag, As, Au, Ba, Co, Cr, Ga, Hg, In, La, Mn, Mo, Ni, Pd, Rb, Sb, Se, Sn, Sr, Tl, U, Y and Zr were below detectable levels for all sample runs.

Table 4-15. Elements, as Measured by the Dilution Tunnel (Site 1).

Parameter	Value							
Units	mg/dscm					%	mg/dscm	
Run Number Date	1 15-Feb-01	2 16-Feb-01	3 20-Feb-01	3 21-Feb-01	Average	RSD	Ambient 22-Feb-01	MDL (2)
Al	1.2E-3	2.1E-4	2.3E-4	2.8E-4	4.9E-4	102	4.6E-4	1.2E-1
Br	ND	ND	1.3E-5	1.8E-5	1.5E-5	23	4.2E-6	1.2E-2
Ca	7.3E-4	2.0E-4	1.4E-4	2.1E-4	3.2E-4	86	4.7E-4	5.5E-2
Cd	2.2E-4	2.8E-4	ND	ND	2.5E-4	17	ND	1.5E-1
Cl	1.5E-4	ND	7.0E-4	1.7E-4	3.4E-4	93	1.7E-3	1.2E-1
Cr	ND	ND	ND	ND	ND	n/a	1.5E-6	2.3E-2
Cu	6.4E-4	8.0E-5	9.4E-5	7.8E-4	4.0E-4	91	1.6E-5	1.3E-2
Fe	8.9E-3	1.5E-4	1.4E-4	2.1E-4	2.4E-3	186	8.3E-4	1.8E-2
K	8.8E-5	ND	9.3E-5	ND	9.1E-5	4	2.7E-4	7.5E-2
Mg	4.9E-4	2.9E-4	6.3E-5	3.3E-4	2.9E-4	60	1.3E-4	0.0E+0
Mn	ND	ND	ND	ND	ND	n/a	1.4E-5	2.0E-2
Na	1.5E-4	3.2E-4	1.2E-3	5.2E-4	5.4E-4	83	5.9E-4	0.0E+0
Ni	ND	ND	ND	ND	ND	n/a	1.3E-6	1.1E-2
P	8.4E-5	ND	9.6E-5	ND	9.0E-5	9	ND	6.9E-2
Pb	ND	ND	ND	5.7E-5	5.7E-5	n/a	1.2E-5	3.7E-2
Rb	ND	ND	ND	ND	ND	n/a	1.1E-6	1.2E-2
S	5.9E-3	8.5E-3	3.3E-3	1.3E-2	7.7E-3	54	4.4E-4	6.1E-2
Si	8.8E-4	4.4E-4	3.1E-4	5.8E-4	5.5E-4	44	1.4E-3	7.7E-2
Sr	ND	ND	ND	ND	ND	n/a	4.9E-6	1.3E-2
Ti	ND	ND	ND	4.2E-5	4.2E-5	n/a	7.5E-5	3.6E-2
Tl	ND	ND	ND	ND	ND	n/a	1.3E-6	3.1E-2
V	ND	ND	3.7E-5	ND	3.7E-5	n/a	6.8E-6	3.1E-2
Zn	5.0E-3	ND	7.3E-5	2.8E-4	1.8E-3	156	3.7E-5	1.3E-2
Zr	ND	ND	ND	ND	ND	n/a	1.0E-6	2.1E-2

(1) No detection limits given. Zeroes treated as non-detect. Data is semi-quantitative.

(2) Method detection limit for Runs 1-4 (dilution ratio 25:1). Ambient sample MDLs are smaller due to MDL- Method Detection Limit

ND- Not detected

n/a- not applicable; only one run within detectable limits.

RSD- Relative standard deviation

Carbonyls (Aldehydes and Ketones)

Aldehydes were captured in a DNPH-impregnated silica gel cartridge. Results are presented in Table 4-16. Formaldehyde, acetaldehyde and valeraldehyde were present at detectable levels in the stack samples; acetone was also present, but the number is biased high by the use of acetone in the same recovery area where the cartridges were stored. Therefore, acetone results are not presented and in the future, precautions will be taken to recover the cartridges in an area away from the PM cyclone recovery area. Only acetaldehyde was detected in the blank, at a level within an order of magnitude of the average stack concentration. A backup cartridge was in place during Run 4 to check for breakthrough. The concentrations detected in the backup are approximately half those in the front sample, indicating that there may be significant breakthrough. Additional backup samples will be taken in future test to determine if breakthrough is a consistent problem.

Table 4-16. Carbonyl (Aldehyde) Results (mg/dscm) (Site 1).

Run	1	2	3	4	4 (Backup)	Average	RSD (%)	Amb
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01	21-Feb-01			22-Feb-01
Formaldehyde	6.6E-2	4.4E-2	3.4E-2	4.3E-2	1.7E-2	4.7E-2	29	1.5E-3
Acetaldehyde	3.6E-2	3.9E-2	4.7E-2	6.6E-2	2.3E-2	4.7E-2	28	1.8E-3
Valeraldehyde	1.6E-2	9.8E-3	1.2E-2	1.2E-2	ND	1.3E-2	21	6.0E-4

Gaseous Precursors

Gaseous ammonia was captured on a citric acid-impregnated cellulose-fiber filter downstream of the quartz filter used for ions and OC/EC analysis. Sulfur dioxide was captured on a potassium carbonate impregnated cellulose-fiber filter downstream of a quartz filter. Results are presented in Table 4-17.

Table 4-17. Secondary PM Gaseous Precursor Results (Site 1).

Parameter	Units	Value						
Run Number	-	1	2	3	4	Average	RSD	Ambient
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
Ammonia	mg/dscm	0.14	0.12	0.17	0.11	0.14	19%	1.1E-3
	lb/hr	0.031	0.026	0.036	0.021	0.029	22%	n/a
Sulfur Dioxide	mg/dscm	16.3	19.8	17.5	20.8	18.6	11%	8.6E-4
	lb/hr	3.5	4.2	3.7	4.1	3.9	8%	n/a

4.2 Refinery Heater Emission Factors

Emission factors from the Site 1 Refinery Heater Test results were determined by dividing the emission rate, in lb/hr, by the measured heat input, in MMBtu/hr, to give pounds per million British thermal unit (lb/MMBtu). Heat input is the product of the measured fuel flow rate and the average fuel heating value (based on fuel grab sample analysis). Average emission factors were determined by averaging detected data. Undetected data were excluded.

4.2.1 Uncertainty

An uncertainty analysis was performed to determine the 95 percent confidence interval and to estimate the upper limit of the measured emission factor and the mass speciation results (ASME, 1990). In the tables that follow, the reported results, the total uncertainty, and a 95 percent confidence upper bound are given for each of the substances of interest. The total uncertainty represents the 95 percent confidence interval based on a two-tailed Student "t" distribution. The 95 percent confidence upper bound estimate is based on the single-tailed Student "t" distribution at the 95 percent confidence level.

4.2.2 Emission Factors

Table 4-18 presents emission factors for primary emissions, including filterable and condensable particulate mass, and elements and ions as measured on the dilution tunnel filters. FPM includes all particulate captured in the in-stack cyclones, probe and filter. Inorganic, organic and total CPM have been corrected in accordance with Method 202 guidelines. The average emission factor for total PM_{2.5} (including CPM) measured using in-stack methods and a purged back-half train is 680 times higher than the emission factor for PM_{2.5} by the dilution tunnel; the total PM_{2.5} emission factor for the in-stack methods with the unpurged train is 220 times higher than the dilution tunnel emission factor. As discussed previously in Section 4, this is believed to be due to sampling and analytical artifacts associated with the CPM measurement method, however the higher CPM data for the purged train is inconsistent with the hypothesis that sulfate is causing an artifact. Therefore, the emission factor derived from the dilution tunnel results is considered the most reliable.

Table 4-18. Primary Emissions- Particulate Mass and Elements (Site 1).

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Particulate Mass	Organic CPM (unpurged train)	1.1E-3	76	1.7E-3
	Inorganic CPM (unpurged train)	6.6E-3	98	1.1E-2
	Total CPM (unpurged train)	7.8E-3	93	1.3E-2
	Organic CPM (purged train)	1.7E-3	43	2.2E-3
	Inorganic CPM (purged train)	2.3E-2	57	3.3E-2
	Total CPM (purged train)	2.5E-2	53	3.5E-2
	Total Filterable PM (Method 17, unpurged train)	5.5E-4	36	7.1E-4
	Total Filterable PM (Method PRE-4, purged train)	9.3E-4	90	1.5E-3
	Filterable PM10 (Method PRE-4, purged train)	6.1E-4	77	9.7E-4
	Filterable PM2.5 (Method PRE-4, purged train)	4.5E-4	76	7.1E-4
	PM2.5 (dilution tunnel)	3.7E-5	33	4.7E-5
Elements (dilution tunnel)	Al	6.5E-7	163	1.4E-6
	Br	1.9E-8	215	3.9E-8
	Ca	4.2E-7	138	8.5E-7
	Cd	3.3E-7	164	6.0E-7
	Cl	4.4E-7	231	1.1E-6
	Cu	5.0E-7	147	1.1E-6
	Fe	3.2E-6	296	1.0E-5
	K	1.2E-7	60	1.6E-7
	Mg	3.8E-7	98	6.5E-7
	Na	6.9E-7	133	1.4E-6
	P	1.2E-7	97	1.8E-7
	Pb	6.7E-8	n/a	n/a
	S	9.6E-6	88	1.6E-5
	Si	7.2E-7	72	1.1E-6
	Ti	4.8E-8	n/a	n/a
	V	4.8E-8	n/a	n/a
	Zn	2.4E-6	388	8.8E-6
Ions (dilution tunnel)	Chloride	2.1E-6	103	3.2E-6
	Nitrate	6.0E-6	71	9.2E-6
	Sulfate	2.5E-5	87	4.1E-5
	Ammonium	1.1E-5	124	2.0E-5

n/a- not applicable; only one run was within detectable limits.

Table 4-19 presents emission factors for OC, EC, total carbon, and SVOCs as measured by the dilution tunnel. SVOC emission factors are low. The average sum of all SVOCs equals 1.6×10^{-5} lb/MMBtu, comprising approximately 25 percent of the total organic carbon. Bibenzene has the highest value, with an emission factor of 4.7×10^{-6} lb/MMBtu. Since the dilution tunnel samples are expected to collect SVOCs which condense in the plume, these results are useful for receptor modeling purposes.

Table 4-19. Primary Emissions- Carbon and SVOCs (Site 1).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Organic Carbon	6.5E-5	32	8.2E-5
Elemental Carbon	7.1E-6	85	1.2E-5
Total Carbon	7.2E-5	32	9.1E-5
Semi-Volatile Organic Compounds (dilution tunnel)			
Naphthalene	4.7E-6	n/a	n/a
2-methylnaphthalene	3.9E-6	134	7.8E-6
1-methylnaphthalene	1.7E-6	130	3.4E-6
1,3+1,6+1,7-dimethylnaphthalene	1.0E-6	103	1.9E-6
2-ethyl-1-methylnaphthalene	7.5E-7	126	1.4E-6
2,6+2,7-dimethylnaphthalene	6.3E-7	105	1.1E-6
1+2-ethylnaphthalene	3.9E-7	93	6.7E-7
Benz(a)anthracene	3.6E-7	230	9.7E-7
1,4+1,5+2,3-dimethylnaphthalene	3.3E-7	400	1.0E-6
9-fluorenone	2.6E-7	48	3.5E-7
Acenaphthylene	2.5E-7	106	3.9E-7
A-trimethylnaphthalene	2.0E-7	100	3.5E-7
Biphenyl	2.0E-7	n/a	n/a
C-dimethylphenanthrene	1.8E-7	66	2.7E-7
C-trimethylnaphthalene	1.7E-7	71	2.6E-7
B-trimethylnaphthalene	1.5E-7	87	2.6E-7
2,3,5-I-trimethylnaphthalene	1.1E-7	94	1.8E-7
Phenanthrene	1.0E-7	93	1.7E-7
E-dimethylphenanthrene	1.0E-7	n/a	n/a
7-methylbenz(a)anthracene	8.7E-8	260	2.4E-7
1-ethyl-2-methylnaphthalene	7.2E-8	66	1.1E-7
J-trimethylnaphthalene	6.8E-8	49	9.6E-8
E-trimethylnaphthalene	6.9E-8	75	1.1E-7
D-dimethylphenanthrene	7.2E-8	n/a	n/a
Benzo(e)pyrene	4.0E-8	n/a	n/a
C-MePy/MeFl	3.9E-8	227	1.0E-7
Fluoranthene	2.4E-8	59	3.5E-8
2-methylphenanthrene	2.1E-8	70	3.3E-8
Benzanthrone	2.1E-8	n/a	n/a
Chrysene	1.6E-8	77	2.5E-8
Benzo(a)pyrene	1.7E-8	n/a	n/a
Pyrene	1.6E-8	114	2.5E-8
D-MePy/MeFl	1.5E-8	165	3.3E-8
2,4,5-trimethylnaphthalene	1.6E-8	n/a	n/a
B-MePy/MeFl	7.7E-9	n/a	n/a
5+6-methylchrysene	7.7E-9	47	1.1E-8
Anthrone	5.8E-9	221	1.5E-8
Benzonaphthothiophene	4.0E-9	n/a	n/a
Anthracene	6.0E-10	n/a	n/a
Sum of All SVOCs	1.6E-5		

n/a- not applicable; only one run was within detection limits.

Emission factors for VOCs obtained from the Tenax samples with carbon number greater than seven are presented in Table 4-20. All VOCs are present at low levels, with benzaldehyde being the most abundant (2.2×10^{-4} lb/MMBtu).

Emission factors for VOCs obtained from the canister samples with carbon number greater than two are presented in Table 4-21. All VOCs are present at low levels, with propene being the most abundant (5.8×10^{-3} lb/MMBtu).

Carbonyl emission factors are presented in Table 4-22. Formaldehyde and acetaldehyde are present at approximately the same levels. The emission factor for formaldehyde (6.1×10^{-5}) is slightly higher than that found in the EPA FIRE 4.23 database (5.5×10^{-5}) for a process gas-fired process heater with no emission controls.

Emission factors for SO₂ and NH₃ are presented in Table 4-23.

4.2.3 PM2.5 Speciation Profiles

Dilution Tunnel

The speciation profile for PM2.5, based on dilution tunnel results, is given in Table 4-24. This table includes all results from the ED-XRF analysis of the dilution tunnel Teflon[®] filters, the ion analysis of the dilution tunnel quartz filters and the OC/EC analysis of the dilution tunnel quartz filters. The mass fractions presented are the ratio of the emission factor of the emitted compound over the sum of the species emission factors.

The average emission factor for the sum of species (1.1×10^{-4} lb/MMBtu) is approximately three times greater than the average emission factor for total PM2.5 mass (3.7×10^{-5} lb/MMBtu, measured gravimetrically). This difference is most likely due to the bias associated with the different analytical methods used to determine the speciation of the mass versus the gravimetric analysis used to measure total PM2.5 mass. In addition, two different types of filters were used: Teflon[®] filters were used for the elemental analysis and particulate mass, while quartz filters were used for OC/EC analysis and ionic analysis. It is possible that variations in particle deposition occurred between the different filters, resulting in a bias. Inhomogeneous deposition

Table 4-20. Secondary Organic Aerosol Precursors (VOCs) from Tenax Samples (Site 1).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Benzaldehyde	2.2E-4	446	7.0E-4
Hexadecanoic acid	1.9E-4	798	9.6E-4
Styrene	9.4E-5	944	5.4E-4
Acetophenone	8.0E-5	492	2.8E-4
Phenol	3.8E-5	554	1.4E-4
Nonanal	2.1E-5	492	7.2E-5
Decanal	1.4E-5	n/a	n/a
m & p-xylene	1.3E-5	96	2.0E-5
Nonane	7.6E-6	285	1.8E-5
m/p-methylphenol	6.4E-6	62	8.9E-6
Ethylbenzene	6.2E-6	400	1.9E-5
Decane	5.3E-6	499	1.9E-5
Heptanal	5.1E-6	n/a	n/a
Biphenyl	5.0E-6	n/a	n/a
Undecane	4.7E-6	n/a	n/a
o-xylene	4.7E-6	169	8.7E-6
Dodecene	3.9E-6	n/a	n/a
Dodecane	3.2E-6	n/a	n/a
m-ethyltoluene	3.2E-6	158	5.8E-6
1-undecene	3.2E-6	n/a	n/a
1,2,4-trimethylbenzene	3.2E-6	241	7.0E-6
Naphthalene	3.0E-6	n/a	n/a
1-nonene	2.5E-6	237	5.6E-6
2,3-benzofuran	2.5E-6	642	1.1E-5
Pentadecane	2.0E-6	268	4.6E-6
1,3-dichlorobenzene	1.9E-6	96	2.8E-6
4-methylstyrene	1.8E-6	690	7.8E-6
C-dimethylindane	1.7E-6	n/a	n/a
2-heptanone	1.7E-6	n/a	n/a
Propylbenzene	1.5E-6	500	5.4E-6
Tetradecane	1.4E-6	n/a	n/a
4-tert-butyltoluene	1.2E-6	n/a	n/a
o-ethyltoluene	1.2E-6	214	2.4E-6
Indene	1.1E-6	n/a	n/a
p-ethyltoluene	1.1E-6	247	2.4E-6
(+/-) - limonene	9.1E-7	62	1.3E-6
1,3,5-trimethylbenzene	8.4E-7	436	2.7E-6
Phenanthrene	7.8E-7	n/a	n/a
2-methylnaphthalene	7.8E-7	n/a	n/a
Tridecane	7.8E-7	n/a	n/a
1,2-diethylbenzene	5.8E-7	179	1.1E-6
5-ethyl-m-xylene	5.5E-7	n/a	n/a
Hexadecane	5.4E-7	499	1.9E-6
1-methylnaphthalene	4.6E-7	437	1.5E-6
4-ethyl-o-xylene	3.8E-7	n/a	n/a
Heptadecane	3.0E-7	n/a	n/a
1,3-diethylbenzene	2.0E-7	n/a	n/a
2-ethyl-p-xylene	2.0E-7	n/a	n/a
1,2,3,4-tetramethylbenzene	2.0E-7	n/a	n/a
1,2-dichlorobenzene	1.6E-7	n/a	n/a
1,2,4,5-tetramethylbenzene	1.3E-7	179	2.6E-7
2-n-propyltoluene	9.8E-8	n/a	n/a
4-n-propyltoluene + 1,4-diethylbenzene	6.7E-8	n/a	n/a

n/a- Not applicable. Only one run within detectable limits.

Table 4-21. Secondary Organic Aerosol Precursors (VOCs) from Canister Samples (Site 1).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
1,1-dimethylcyclohexane	1.2E-5	521	4.4E-5
1,2,3,4-tetramethylbenzene	1.5E-5	65	2.3E-5
1,2,3,5-tetramethylbenzene	2.8E-5	66	4.2E-5
1,2,3-trimethylbenzene	1.3E-5	189	3.1E-5
1,2,4,5-tetramethylbenzene	1.4E-5	80	2.3E-5
1,2,4-trimethylbenzene	4.5E-5	51	6.4E-5
1,2-diethylbenzene	2.1E-5	102	3.7E-5
1,3,5-trimethylbenzene	1.8E-5	63	2.7E-5
1,3-butadiene	6.9E-6	102	1.2E-5
1,3-diethylbenzene	7.7E-5	95	1.3E-4
1,3-dimethylcyclopentane	2.0E-5	87	3.4E-5
1,4-diethylbenzene	2.8E-5	40	3.8E-5
1-butene	2.6E-4	96	4.5E-4
1-hexene	5.9E-5	210	1.4E-4
1-methylcyclopentene	5.4E-6	120	1.0E-5
1-methylindan	8.9E-6	102	1.5E-5
1-pentene	7.9E-5	105	1.4E-4
2,2,4-trimethylpentane	4.9E-5	79	7.9E-5
2,2,5-trimethylhexane	5.9E-5	n/a	n/a
2,2-dimethylbutane	1.8E-5	106	3.3E-5
2,3,4-trimethylpentane	1.9E-5	64	2.8E-5
2,3,5-trimethylhexane*	1.2E-3	119	2.4E-3
2,3-dimethylbutane	3.3E-5	100	5.8E-5
2,3-dimethylhexane	8.5E-6	572	3.3E-5
2,3-dimethylpentane	2.4E-5	85	4.0E-5
2,4,4-trimethyl-1-pentene	1.6E-5	104	2.9E-5
2,4-dimethylhexane	1.5E-6	28	1.9E-6
2,4-dimethylpentane	2.1E-5	80	3.4E-5
2,5-dimethylhexane	1.0E-5	79	1.6E-5
2,5-dimethylheptane	9.3E-6	75	1.5E-5
2,6-dimethylheptane	6.4E-6	49	8.9E-6
2,6-dimethyloctane	3.1E-5	78	4.9E-5
2-methyl-1-butene	3.0E-5	106	5.4E-5
2-methyl-1-pentene	4.1E-6	110	7.6E-6
2-methyl-2-butene	2.9E-5	151	6.2E-5
2-methyl-2-pentene	7.7E-6	68	1.2E-5
2-methylheptane	1.9E-5	69	2.9E-5
2-methylhexane	3.2E-5	82	5.2E-5
2-methylpentane	9.8E-5	99	1.7E-4
3,3-dimethylheptane	4.2E-6	114	7.8E-6
3,3-dimethylpentane	5.0E-6	79	8.0E-6
3,6-dimethyloctane	3.8E-5	65	5.7E-5
3-ethylpentane	2.1E-5	110	3.9E-5
3-methyl-1-butene	1.9E-5	102	3.3E-5
3-methyl-2-pentene	5.9E-6	112	1.0E-5
3-methylheptane	1.3E-5	63	1.9E-5
3-methylhexane + pentanal	4.5E-5	75	7.1E-5
3-methyloctane	1.1E-5	51	1.5E-5
3-methylpentane	8.5E-5	138	1.7E-4

Table 4-21. Secondary Organic Aerosol Precursors (VOCs) from Canister Samples (Site 1)
(Continued).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
4,4-dimethylheptane	5.9E-6	38	7.9E-6
4-methylheptane	5.8E-6	112	1.1E-5
4-methylhexene	2.6E-6	117	4.9E-6
Acetone	1.4E-4	192	3.3E-4
Acetylene	1.8E-4	79	3.0E-4
Benzaldehyde	2.3E-6	92	3.8E-6
Benzene	1.1E-4	77	1.8E-4
Beta-pinene	2.0E-5	77	3.2E-5
C10 aromatic 1	6.6E-6	50	9.3E-6
C10 aromatic 2	9.3E-6	46	1.3E-5
C10 aromatic 4	3.6E-6	71	5.5E-6
C10 aromatic 5	1.3E-5	59	2.0E-5
C10 aromatic 6	1.1E-5	153	2.2E-5
C10 olefin 2	6.1E-5	52	8.6E-5
C10 paraffin a	4.8E-5	103	8.6E-5
C10 paraffin c	5.1E-5	94	8.7E-5
C11 aromatic 1	7.9E-6	113	1.4E-5
C11 paraffin a	6.3E-6	53	8.5E-6
C-2-butene	1.9E-4	69	2.9E-4
C-2-hexene	7.2E-6	108	1.1E-5
C-2-pentene	1.8E-5	95	3.1E-5
C-3-hexene	6.9E-6	30	8.9E-6
C-3-hexene	6.3E-6	180	1.4E-5
C6 olefin 1	3.9E-6	38	5.2E-6
C7 olefin 1	3.8E-6	147	7.7E-6
C7 olefin 2	2.6E-6	53	3.5E-6
C8 olefin 1	5.2E-6	66	7.9E-6
C8 olefin 2	1.5E-6	53	2.0E-6
C8 olefin 3	1.3E-5	98	2.4E-5
C8 paraffin 2	1.0E-5	53	1.4E-5
C9 olefin 2	5.9E-6	85	9.7E-6
C9 olefin 3	1.1E-5	176	2.4E-5
C9 olefin 4	5.4E-6	54	7.8E-6
C9 paraffin 1	6.3E-6	70	9.8E-6
C9 paraffin 2	2.1E-6	68	3.3E-6
C9 paraffin 3	3.4E-6	71	5.3E-6
Chlorobenzene	1.8E-6	69	2.8E-6
cis-3-methyl-2-pentene	3.9E-6	66	5.9E-6
Cyclohexane	2.2E-3	166	5.0E-3
Cyclohexene	2.2E-6	116	4.1E-6
Cyclopentane	4.5E-5	85	7.5E-5
Cyclopentene	1.0E-5	85	1.7E-5
Decene-1*	2.3E-3	45	3.2E-3
Dodecene-1	4.4E-6	127	8.4E-6
Ethane	7.0E-4	69	1.1E-3
Ethanol	1.8E-6	n/a	n/a
Ethene	4.1E-4	136	8.3E-4
Ethylbenzene	3.0E-5	50	4.2E-5
Heptene-1	1.4E-5	586	5.6E-5

Table 4-21. Secondary Organic Aerosol Precursors (VOCs) from Canister S amples (Site 1) (Continued).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Hexanal	7.4E-5	69	1.1E-4
Indan	8.6E-6	32	1.1E-5
Indene	6.5E-6	34	8.5E-6
Isobutane	2.2E-3	86	3.7E-3
Iso-butene	2.7E-4	96	4.6E-4
Isobutylbenzene	4.3E-5	42	5.8E-5
Isopentane	7.2E-4	109	1.3E-3
Isopropylbenzene	4.4E-6	104	7.8E-6
Isopropylcyclohexane	7.5E-6	68	1.2E-5
Isopropyltoluene	9.7E-6	58	1.4E-5
Limonene	5.9E-6	67	9.0E-6
m- & p-xylene	1.2E-4	54	1.7E-4
Methanol	9.2E-5	212	2.3E-4
Methylcyclohexane	3.9E-5	65	5.9E-5
Methylcyclopentane	3.1E-4	171	7.0E-4
m-ethyltoluene	4.0E-5	54	5.7E-5
MTBE	6.9E-6	n/a	n/a
Naphthalene	1.9E-5	42	2.6E-5
n-butane	4.5E-3	110	8.2E-3
n-decane	6.6E-5	53	9.5E-5
n-dodecane	4.9E-5	95	8.5E-5
n-heptane	4.0E-5	60	6.0E-5
n-hexane	9.3E-4	225	2.5E-3
n-nonane	2.0E-5	61	2.9E-5
n-octane	2.5E-5	31	3.2E-5
Nonene-1	3.3E-6	128	6.2E-6
n-pentane	1.8E-4	104	3.2E-4
n-propylbenzene	1.9E-5	47	2.7E-5
n-undecane	7.1E-5	61	1.1E-4
Octanal	1.0E-4	112	1.9E-4
Octene-1	8.1E-6	32	1.1E-5
o-ethyltoluene	1.6E-5	90	2.7E-5
o-xylene	5.0E-5	47	7.0E-5
p-ethyltoluene	2.4E-5	66	3.6E-5
Propane	2.5E-3	79	4.1E-3
Propene	5.8E-3	103	1.0E-2
sec-butylbenzene	2.7E-6	420	8.4E-6
Styrene + heptanal	7.9E-5	51	1.1E-4
t-2-butene	1.8E-4	97	3.2E-4
t-2-hexene	8.0E-6	88	1.3E-5
t-2-pentene	3.4E-5	96	5.8E-5
t-3-heptene	4.7E-6	109	8.3E-6
Toluene	5.0E-4	37	6.7E-4
Total Identified NMHC	6.7E-3	80	1.1E-2
Unidentified	3.2E-4	44	4.4E-4

n/a- Not applicable. Only one run within detectable limits.

Table 4-22. Carbonyl (Aldehyde) Emission Factors (Site 1).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Formaldehyde	6.1E-5	127	1.2E-4
Acetaldehyde	6.0E-5	132	1.2E-4
Valeraldehyde	1.6E-5	177	3.8E-5

Table 4-23. Secondary Particulate Precursors- NH₃ and SO₂ (Site 1).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
NH ₃	1.3E-4	35	1.6E-4
SO ₂	0.024	26	0.029

Table 4-24. Speciation Profile for Primary Emissions- Dilution Tunnel Results (Site 1).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
OC	63	47	87
Ammonium	11	134	22
S	9.1	95	16
EC	6.6	92	11
Nitrate	5.9	79	9.4
Fe	2.5	298	8.0
Chloride	2.2	203	4.6
Zn	1.9	392	6.9
Si	0.66	80	1.1
Al	0.56	167	1.3
Cu	0.45	151	0.95
Ca	0.37	142	0.76
Cd	0.30	240	0.65
K	0.12	185	0.24
P	0.12	200	0.24
Pb	0.06	n/a	n/a
V	0.06	n/a	n/a
Ti	0.05	n/a	n/a
Br	0.02	277	0.05

n/a- Not applicable. Only one run within detectable limits.

1- Mass fraction is emission factor of species divided by emission factor of sum of species. Average speciated mass was greater than average total PM_{2.5} mass measured on the dilution tunnel filter.

on the filter could also cause a bias. The OC/EC analysis and ion analysis each take only part of the filter for analysis, and the total mass on the filter is normalized assuming that this mass is evenly distributed over the collection area.

Figure 4-1 shows the data presented in Table 4-24. The majority of the mass (63 percent) is composed of organic carbon, with ammonium being the next most abundant constituent (11 percent). Compounds with all runs below detectable levels are not included in the figure. Sulfate, chlorine, sodium and magnesium were all measured at detectable levels, but are not included in the sum of species, and are therefore not included in the figure.

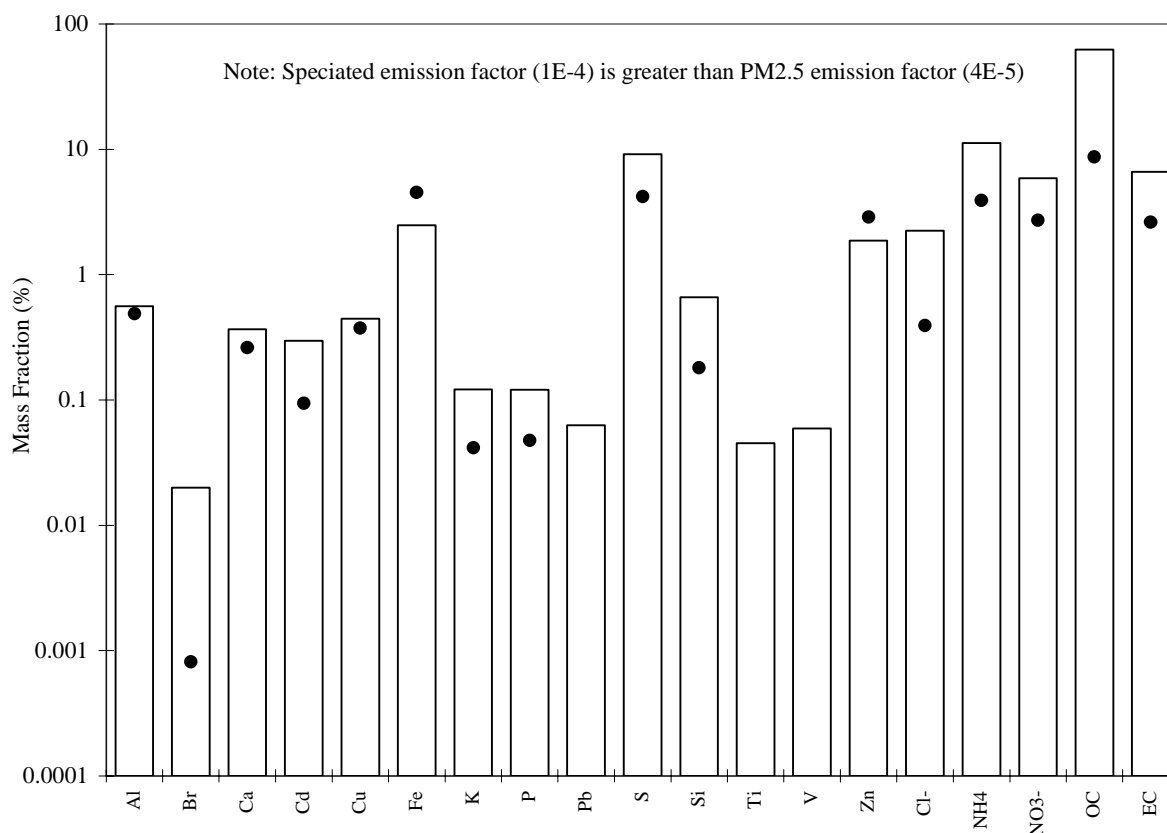


Figure 4-1. PM_{2.5} speciation, as measured by the dilution tunnel (Site 1).

Organic Aerosols

Table 4-25 shows the organic aerosol speciation profile, expressed as a mass fraction. This mass fraction is determined by dividing the average emission factor of the emitted quantity by the average emission factor of total organic carbon, both in units of lb/MMBtu. The speciated

Table 4-25. Organic Aerosol Speciation Profile (Site 1).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
Naphthalene	5.5	n/a	n/a
2-methylnaphthalene	5.4	138	11.09
1-methylnaphthalene	2.4	133	4.91
1,3+1,6+1,7-dimethylnaphthalene	1.5	108	2.76
2-ethyl-1-methylnaphthalene	1.1	134	2.09
2,6+2,7-dimethylnaphthalene	0.91	109	1.67
1+2-ethylnaphthalene	0.57	98	1.00
Benz(a)anthracene	0.60	232	1.64
1,4+1,5+2,3-dimethylnaphthalene	0.45	425	1.40
9-fluorenone	0.40	65	0.59
Acenaphthylene	0.34	180	0.67
A-trimethylnaphthalene	0.29	105	0.52
Biphenyl	0.24	n/a	n/a
C-dimethylphenanthrene	0.27	79	0.43
C-trimethylnaphthalene	0.25	77	0.40
B-trimethylnaphthalene	0.23	92	0.39
2,3,5+I-trimethylnaphthalene	0.16	99	0.28
Phenanthrene	0.16	98	0.27
E-dimethylphenanthrene	0.12	n/a	n/a
7-methylbenz(a)anthracene	0.14	263	0.40
1-ethyl-2-methylnaphthalene	0.11	73	0.17
J-trimethylnaphthalene	0.11	58	0.16
E-trimethylnaphthalene	0.10	82	0.17
D-dimethylphenanthrene	0.08	n/a	n/a
Benzo(e)pyrene	0.07	n/a	n/a
C-MePy/MeFl	0.06	230	0.17
Fluoranthene	0.04	67	0.06
2-methylphenanthrene	0.03	77	0.05
Benzanthrone	0.02	n/a	n/a
Chrysene	0.02	89	0.04
Benzo(a)pyrene	0.02	n/a	n/a
Pyrene	0.02	184	0.04
D-MePy/MeFl	0.02	168	0.06
2,4,5-trimethylnaphthalene	0.02	n/a	n/a
B-MePy/MeFl	0.01	n/a	n/a
5+6-methylchrysene	0.01	56	0.02
Anthrone	0.008	225	0.02
Benzonaphthothiophene	0.005	n/a	n/a
Anthracene	0.001	n/a	n/a

n/a- Not applicable. Only one run was within detectable limits.

1- Mass fraction expressed as a percent of total organic carbon.

organic carbon, measured as SVOCs, accounts for approximately 22 percent of the total organic carbon. The data from Table 4-25 are shown in Figure 4-2. As can be seen on the figure, the most abundant fraction of the speciated organic aerosol is naphthalene (5.5 percent), followed by 2-methylnaphthalene (5.4 percent).

Method PRE-4/202

Table 4-26 shows the speciation profile of the PM_{2.5} mass as measured by Method PRE-4/202 for the Standard Method results. Mass fraction is the ratio of the measured quantity to the total PM_{2.5} mass (filterable and condensable particulate). In this table, total condensable particulate has been subdivided into its respective organic and inorganic fractions for illustrative purposes. Inorganic condensable particulate has been further subdivided to show the amount of PM_{2.5} mass accounted for by sulfate.

The data from Table 4-26 are shown in Figure 4-3. As can be seen from the figure, nearly all of the PM_{2.5} mass comes from CPM (98 percent). The large majority of CPM is contained in the inorganic fraction, which accounts for 90 percent of the total PM_{2.5} mass.

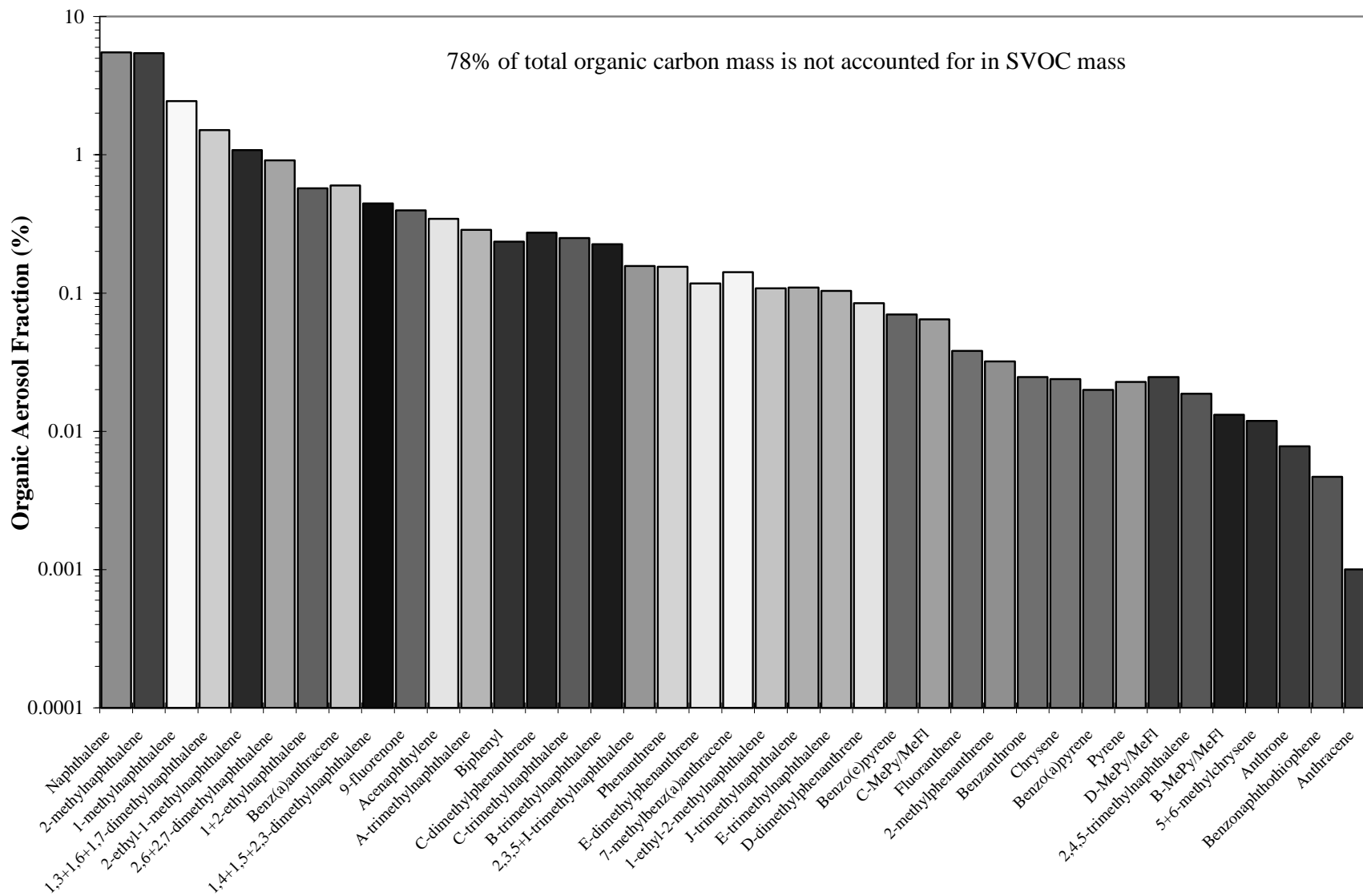


Figure 4-2. Organic aerosol speciation (Site 1)

Table 4-26. Speciation Profile for PM2.5 Measured by Method PRE-4/202 (Site 1).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
Filterable PM2.5	1.8	93	3.1
Total Condensible PM	98	76	155
Organic CPM	7.2	68	11
Inorganic CPM	90	78	144
- Sulfate (as SO ₄ ⁼)	73	73	114
Total	100		

(1) Mass fraction is percent of total PM2.5 (filterable and condensible).

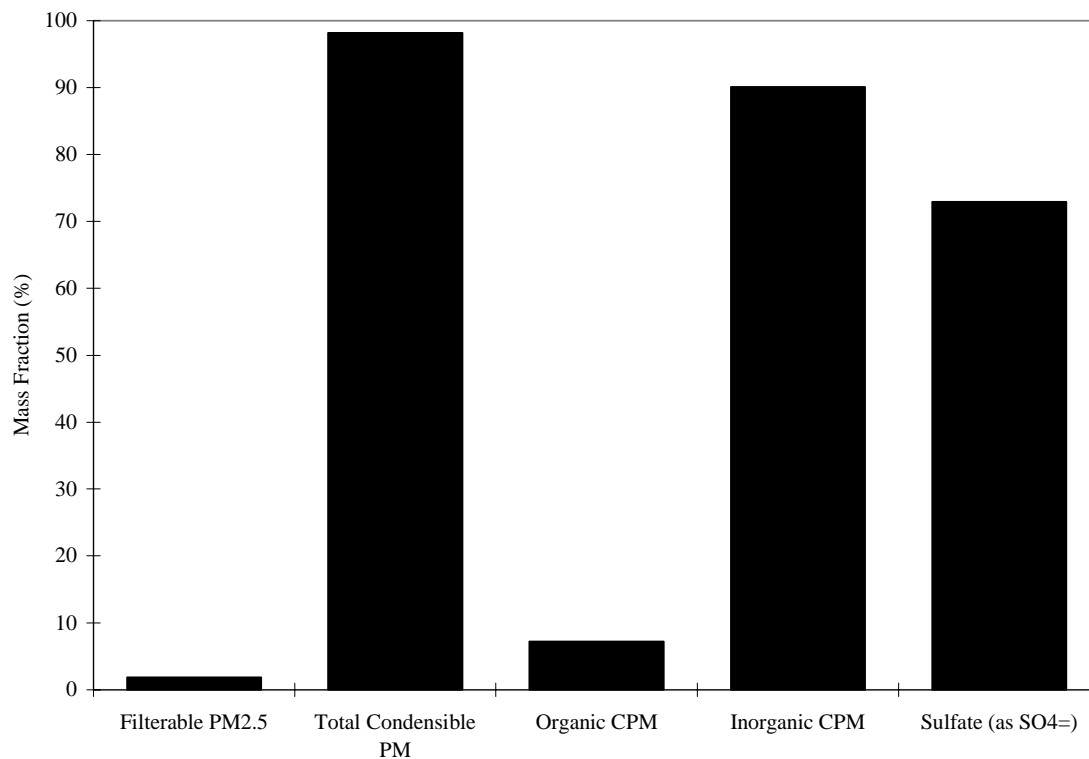


Figure 4-3. Method PRE-4/202 PM2.5 mass speciation profile (Site 1).

Section 5 CONCLUSION

PM 2.5 emissions from a refinery gas-fired process heater measured by the dilution tunnel technique were found to be more three orders of magnitude lower than that measured by conventional in-stack methods (Methods PRE-4/202). In fact, PM 2.5 concentrations found in the stack emissions were approximately equal to those measured concurrently in nearby ambient air.

Dilution tunnel sampling is designed to capture filterable matter and any aerosols that condense under simulated stack plume conditions. Stack gas is cooled to ambient temperatures, typically 60-70 °F in these tests, in the dilution tunnel and samples are then collected from the diluted air mass. Conventional in-stack methods are designed to collect particles that are filterable at the stack temperature along with capturing those likely to condense in ambient air by collecting them in a series of aqueous impingers placed in an ice bath. The gas temperature leaving the impingers is typically 55-65 °F; thus, both systems cool the sample gas to similar final temperatures. However the in-stack methods cool the sample rapidly without dilution by quenching the gas sample in water maintained at near freezing temperature, while the dilution tunnel cooled the sample more slowly by mixing it with ambient air. Since aerosol condensation mechanisms depend on temperature, concentration, residence time and other factors, it is not surprising that the results of the two methods differ. However, mechanistic variations alone cannot account for the magnitude of the difference observed in these tests.

Filterable PM 2.5 measured by the in-stack method (4.5 E-4 lb/MMBtu) is an order of magnitude higher than the dilution tunnel value of 3.7 E-5 lb/MMBtu . In fact, 98 percent of the mass found by Method PRE-4/202 was contained in the condensable fraction collected in the impingers. This is similar to earlier test results on gas-fired units (England et al., 2000). A review of those data led us to suspect the validity of the conventionally obtained data on condensables and initiate a more extensive analysis of this fraction in this study than that prescribed by Method 202. Most of the inorganic CPM mass for both the purged and unpurged trains appears to be composed of sulfate and ammonium, with small contributions from sodium and calcium (Figure 5-1). When all species are summed, the total mass exceeds the inorganic CPM mass for both the

purged (109 percent of inorganic CPM) and the unpurged (130 percent of inorganic CPM) trains. The large sulfate content is expected since the sulfur content of the fuel gas is moderate (3 ppmv H_2S , with a total reduced sulfur content of 200 ppm as H_2S). SO_2 stack emissions measured by the dilution tunnel averaged approximately 7 ppm. The extensive instrumental analysis (discussed in Section 4) of the impinger solutions does not find any significant levels of other metals. Although the difference of the measurements from the two Method 202 trains is an order of magnitude, the speciation of each train is similar, as seen in the two pie charts. This similarity yields few clues to the reason for the anomalous results. Additional tests of the effects of purging will be conducted under more controlled conditions at a test facility to attempt to better understand the cause for the purged train having higher CPM.

Table 5-1 presents a comparison of the sulfate measurements, expressed as sulfate ion in mg/dscm. The levels in the impinger aliquot from the purged train are approximately an order of magnitude greater than those from the unpurged train. The levels in the unpurged train are more consistent with previous tests of gas-fired units. The sulfate measured in the purged Method 202 aliquot accounts for approximately 50 percent of the SO_2 (as SO_4^-) measured by the potassium carbonate-impregnated cellulose-fiber filter downstream of the dilution tunnel. In turn, the SO_2 measured by the dilution tunnel accounts for approximately half of the sulfur from the fuel gas. Compared to the measured SO_2 value, the sulfate levels measured by the dilution tunnel account for approximately 0.07 percent of the SO_2 in the flue gas and are an order of magnitude greater than those measured in the ambient sample.

The formation of artifact sulfate caused by SO_2 absorption in the aqueous solutions appears likely. Both SO_2 and oxygen are soluble in water and the dissolved H_2SO_3 can slowly oxidize to sulfate. This is implicitly recognized by Method 202 which recommends purging the impingers with nitrogen (air is also acceptable) to minimize this bias. Method 202 also provides the option of omitting the post test purge if the pH of the impingers is above 4.5; while the pH of the impingers met this criterion in our test, we performed the nitrogen purge anyway. However, earlier studies of systems having SO_2 levels of approximately 2000 ppm show that that these artifacts occur in spite of post-test purging (Filadelfia and McDaniel, 1996).

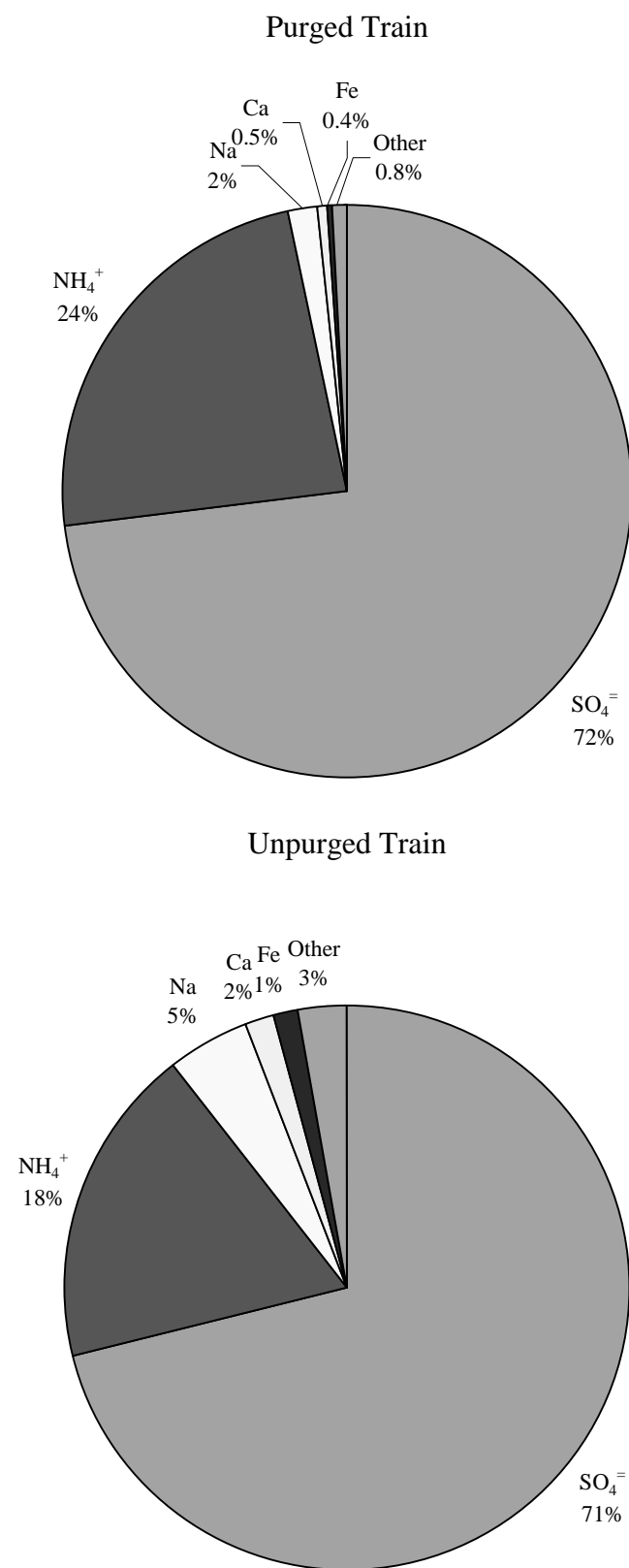


Figure 5-1. Inorganic CPM residue speciation results.

Table 5-1. Comparison of Sulfate Measurements (mg/dscm).

	Run 1	Run 2	Run 3	Run 4	Average
Impinger aliquot (M202) – purged	18.7	10.7	10.6	15.2	13.8
Method 202 residue – purged					
Impinger aliquot (M202) – unpurged	1.71	0.38	1.64	1.18	1.23
Method 202 residue – unpurged					
Dilution tunnel	0.014	0.027	0.009	0.033	0.02
Dilution tunnel SO ₂ measurement (as SO ₄ ²⁻)	24.4	29.8	26.3	31.2	27.9
Ambient (1)	0.0013	--	--	--	0.0013
Total reduced sulfur in fuel (as SO ₄ ²⁻)	45.5	77.0	55.1	58.5	59.0

(1) One ambient sample taken on separate day.

Previous laboratory scale experiments evaluated the potential bias at low SO₂ concentrations (Wien, 1999). The experiments passed simulated combustion gas containing representative amounts of O₂, CO₂, N₂, NO_x, and SO₂ through Method 202 impinger trains. No condensable substances were added. Tests were performed both with and without post-test nitrogen purges for 1-hour and 6-hour sampling runs for mixtures containing 0, 1, and 10 ppm SO₂.

Significant amounts of sulfate, proportional to the SO₂ concentration in the gas, were found to be present in impingers that had not been purged. However, while the post-test purge definitely reduced the sulfate concentrations it did not eliminate artifact formation. Purging was less efficient for the 6-hour runs relative to the 1-hour runs, indicating that most of the SO₂ oxidation occurs within this period. This result shows that the sulfate, and hence most of the condensable particulate collected by Method 202 in our field test results come from this mechanism of artifact sulfate formation from dissolved SO₂. The paired purged and unpurged train results are completely opposite from the results of previous tests presented here, however, and are not readily explained. Further investigation is underway to replicate this experiment.

Recently Corio and Sherwell (2000) reviewed emissions data collected from fossil fuel fired units by Method 201A/202 and raised the question of artifact formation. Table 5-2 presents some of their data (Lakewood Cogeneration and Kamite Milford units) along with data collected by the DOE PM 2.5 program for gas-fired sources from this program (Site 1) and from previous test programs.(Sites A, B, and C). These data compare results from the filterable and

condensable particulate fractions, along with the composition of CPM, for a natural gas-fired boiler and several natural gas-fired turbines.

Table 5-2. Comparison of Data from Corio and Sherwell (2000) and PM2.5 Program Data.

Source	Unit Type	Filterable PM		Condensable PM		Makeup of CPM	
		lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10	Inorganic Fraction (% of Total CPM)	Organic Fraction (% of Total CPM)
Lakewood Cogeneration	Natural Gas-fired Boiler	0.0019	46	0.0022	54	0.0015 (66)	0.00076 (34)
Lakewood Cogeneration – Unit #1	Natural Gas-fired Turbine	0.00021	14	0.0012	86	0.0010 (81)	0.00023 (19)
Lakewood Cogeneration – Unit #2	Natural Gas-fired Turbine	0.00052	33	0.0011	67	0.00084 (78)	0.00024 (22)
Kamine Milford ¹	Natural Gas-fired Turbine	0.0132	56	0.0105	44	0.0045 (43)	0.0060 (57)
Kamine Milford ²	Natural Gas-fired Turbine	0.0015	12	0.0112	88	0.0067 (60)	0.0045 (40)
Kamine Milford ³	Natural Gas-fired Turbine	0.0012	10	0.0107	90	0.0079 (74)	0.0028 (26)
Kamine Milford ⁴	Natural Gas-fired Turbine	0.0014	12	0.0100	88	0.0066 (66)	0.0034 (34)
Site A	Refinery Gas-fired Boiler	0.00016	2	0.0097	98	0.0091 (94)	0.00064 (6)
Site B	Refinery Gas-fired Process Heater	0.00064	12	0.0046	88	0.0048 (97)	0.00024 (3)
Site C	Natural Gas-fired Steam Generator	0.00008	6	0.0012	94	0.00052 (44) ⁵	0.00048 (41) ⁵
Site 1 (this program)	Refinery Gas-fired Process Heater	0.00061	3	0.025	97	0.023 (92) ⁵	0.0017 (7) ⁵

¹ Steam injection (SI) on, waste heat recovery boiler (WHRB) off.

² SI off, WHRB off.

³ SI on, WHRB on.

⁴ SI off, WHRB on.

⁵ Remaining CPM mass accounted for by back-half filter and was not characterized.

As can be seen in Table 5-2, the CPM data from Site 1 presented in this report are higher than data collected at other gas-fired combustion units. However, the filterable fraction is comparable to the other refinery gas-fired process heater (Site B) tested as part of the API PM2.5 program.

The particulate emission factors obtained using the Method PRE-4/202 trains are in general agreement with those found in the EPA's AP-42 emission factor database (EPA, 1998) for

natural gas-fired external combustion devices (Table 5-3). Since the EPA results were obtained using the same method, a similar bias is likely in those data. The condensable catch is higher for this test (Site D) than that reported in AP-42 (0.025 versus in 0.0056 lb/MMBtu in AP-42), and is not explainable. Nevertheless, the semi-quantitative agreement of our results with those presented in the EPA database provides additional confidence in the validity of the results found here.

Table 5-3. Comparison of EPA AP-42 Database and PM2.5 Program Data.

Source	Unit Type	Total PM10 lb/MMBtu	Filterable PM		Condensable PM	
			lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10
AP-42	Natural Gas Combustion	0.0075	0.0019	25	0.0056	75
Site A	Refinery Gas-fired Boiler	0.0099	0.00016	2	0.0097	98
Site B	Refinery Gas-fired Process Heater	0.0052	0.00064	12	0.0046	88
Site C	Natural Gas-fired Steam Generator	0.0013	0.00008	6	0.0012	94
Site 1 (this program)	Refinery Gas-fired Process Heater	0.026	0.00061	3	0.025	97

These results show that traditional source testing methods, such as EPA Method 202, probably overestimate particulate mass emissions by erroneously determining high levels of condensable particulate sulfate. In addition, this method may also overestimate the condensable organic fraction. The low filterable PM results indicate that the actual mass collected on the filters was at, or below, the practical limits of the method as practiced in these tests. Because dilution tunnels provide conditions that more closely simulate true atmospheric condensation conditions, as compared to impinger condensation, results obtained by this technique are more representative of the actual particulate emissions from gas-fired combustion sources such as this boiler.

5.1 Potential Emissions Marker Species

The results obtained using the dilution tunnel are believed to provide the best representation of the chemical species present in the stack gas emissions. Ions, carbon, and other elements were detected in both stack and ambient air samples. A comparison of the observed concentrations of

these species in ambient and stack samples can provide an indication of which species are considered good markers of natural gas combustion for this source.

PM_{2.5} mass, Ca, Cl, K, Na, Si, Ti and chloride (Cl⁻) concentrations are higher in the ambient air sample than for the in-stack sample (Figure 5-2), therefore, it is questionable whether these species originate from the combustion process. Cr, Mn, Ni, Rb, Sr, Tl, and Zr were detected in ambient air but not in stack emissions (n.b., the detection levels for in-stack samples are approximately 6 times higher than those for ambient air samples). Other species cannot reliably be distinguished because their in-stack concentrations are within a factor of ten from the minimum method detection limits (Figure 5-3); these include: Al, Br, Ca, Cd, Cl, K, P, Pb, Si, Ti, V, chloride, nitrate, ammonium, OC, and EC. The average concentrations of all other species except Cu, S, Zn, and sulfate are within a factor of ten of their respective ambient air concentrations. Subtraction of the ambient from in-stack concentrations provides an indication of which species can be considered to be emissions markers. Ignoring species found near detection limits, the resulting emissions profile (Figure 5-4) suggests that these are S, sulfate, Fe, and Zn.

The uncertainty of several of these values is large, as reflected in the high standard deviations, casting doubt on any of the species being definitively used as an emissions marker. The sum of the species shown in Figure 5-4 comprises 366 percent of the PM_{2.5} mass. Other compounds were present at lower levels but the low concentrations and high or unknown standard deviations associated with these suggest that they may not be reliable markers.

Another potentially useful marker for source emissions is the organic emissions profile. All of the SVOCs detected were present at low concentrations. All SVOCs measured by the dilution tunnel, and present at detectable levels, were found at concentrations 10 times greater than ambient levels. Total SVOCs accounts for approximately 25 percent of the OC measured by the dilution tunnel indicating the presence of unspciated organics. This large difference is at least partly due to the difference in analytical methods since the TOR method defines OC somewhat arbitrarily, as well as by the presence of organics that are not quantifiable by the methods used in this study.

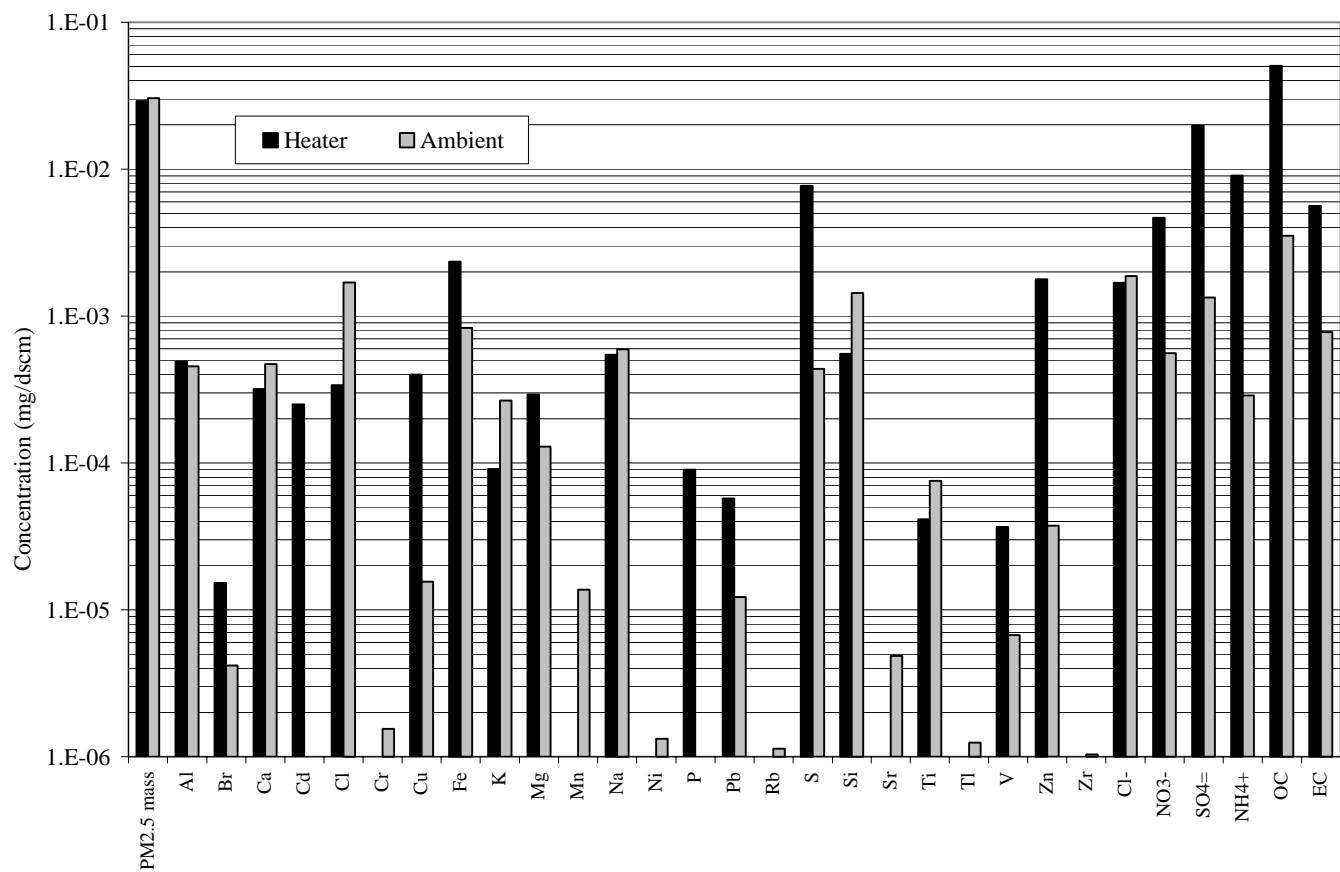


Figure 5-2. Mass speciation for dilution tunnel ambient and stack samples (Site 1).

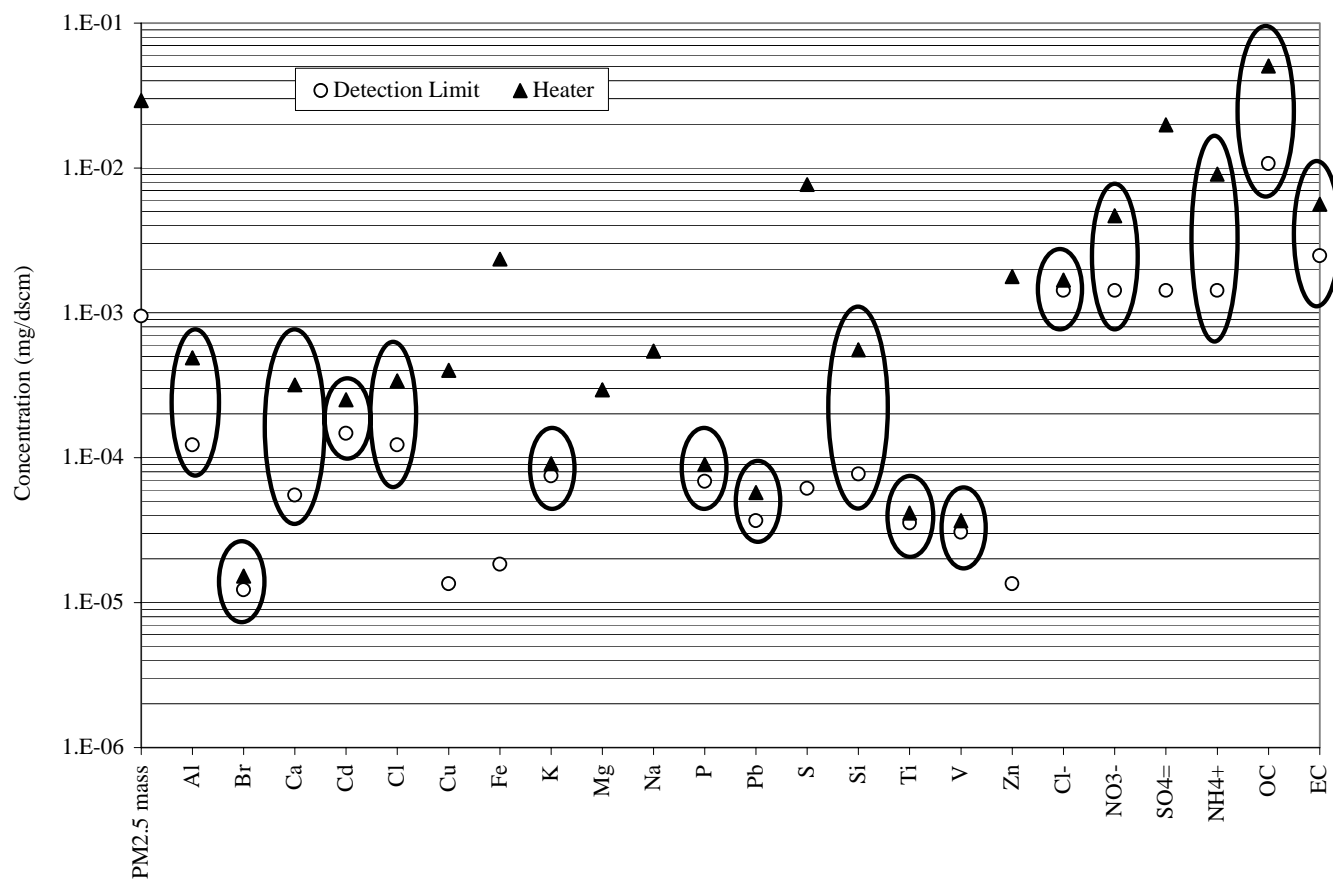


Figure 5-3. Comparison of average sample concentration and detection limits (Site 1).

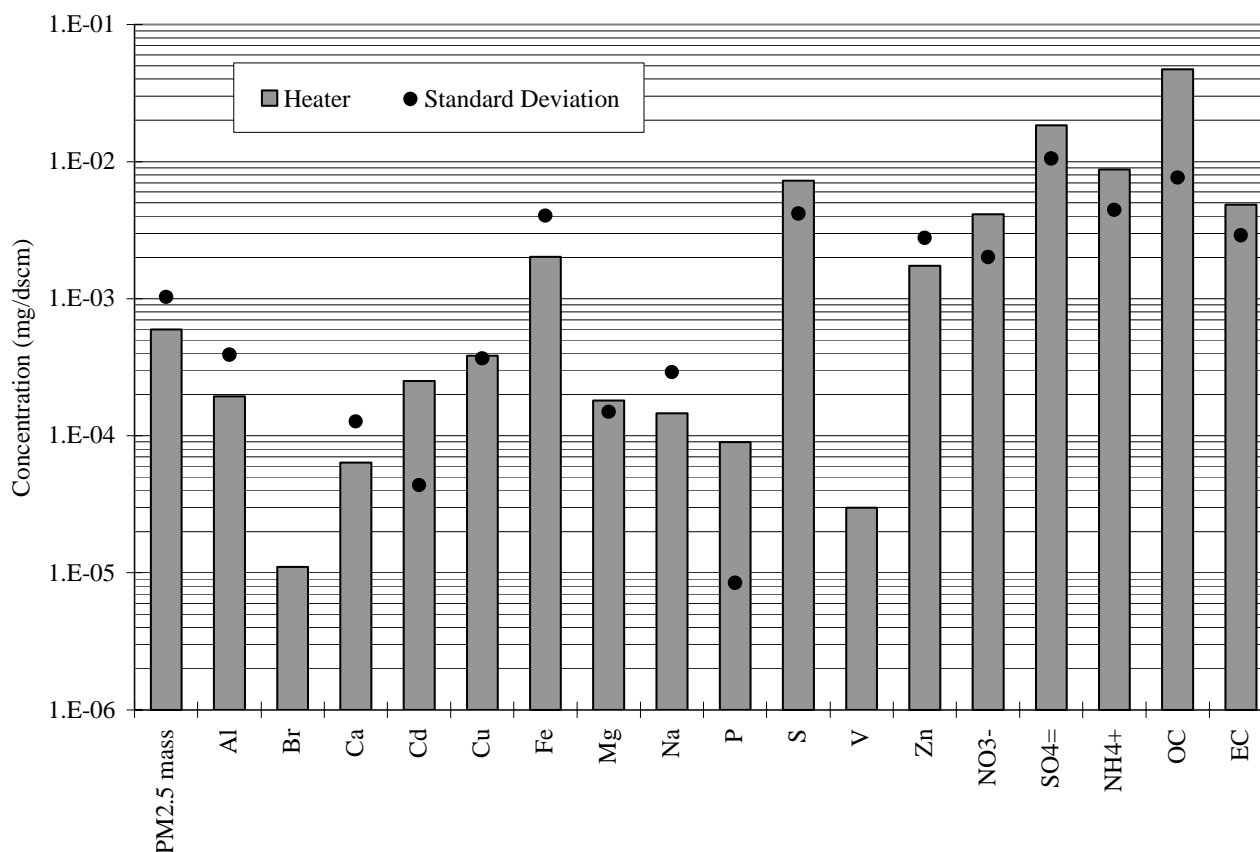


Figure 5-4. Average sample concentration minus ambient concentration (Site 1).

Organic carbon emissions for Site 1 were within an order of magnitude of those found at Site B studied earlier in the API PM2.5 project (Table 5-4), and lower than those from Sites A and C. In contrast, measurable SVOC emissions at Site 1 were approximately 22 times higher than those at Site B, resulting in a greater percentage of OC being speciated. VOC emissions from Site 1 were greater than all other sites to date.

Table 5-4. Average Organic Aerosol Emission Factor Comparison (lb/MMBtu).

Source	Unit Type	Organic Carbon	Elemental Carbon	Total Carbon	Sum of All SVOCs	Sum of All VOCs
Site A	Refinery Gas-fired Boiler	1.5E-4	9.4E-5	2.5E-4	4.1E-6	1.6E-4
Site B	Refinery Gas-fired Process Heater	2.8E-5	1.9E-5	3.4E-5	6.6E-7	4.0E-4
Site C	Natural Gas-fired Steam Generator	2.3E-4	9.2E-6	2.4E-4	1.5E-5	4.1E-5
Site 1 (this program)	Refinery Gas-fired Process Heater	6.5E-5	7.1E-6	7.2E-5	1.6E-5	7.6E-4*

* Does not include VOCs from canister samples

Elevated levels of organic compounds in the stack samples as compared to levels detected in the blank and the ambient air indicate that potential marker species are more likely to be found within the volatile and semivolatile organic compounds. For Site 1, all SVOCs were at least 10 times greater than levels in the ambient air, and only two were within ten times the levels in the field blank. In particular, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, and 1,3+1,6+1,7-dimethylnaphthalene are present at elevated concentrations relative to the other SVOCs, and might be potential marker species. However, motor vehicles are also predominant sources of dimethylnaphthalenes and methylnaphthalenes. Because the ambient air was only sampled on one day, it is possible that elevated levels of these compounds were present in the ambient air during source sampling that were not present when the ambient sample was taken. In addition, the relative concentrations of these compounds may not be unique enough to clearly distinguish this source from other external combustion sources.

Volatile organic species found at levels significantly different to the ambient air include n-benzaldehyde, styrene, and acetophenone, which may be potential marker species. More comparison to existing speciation profiles is necessary to gauge the uniqueness of the profile produced by this test. In addition, further testing of similar sources is recommended to provide a more robust basis for the emission factors and speciation profiles described herein.

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LIST OF ACRONYMS AND ABBREVIATIONS

$\mu\text{g}/\text{cm}^2$	micrograms per square centimeter
AC	automated colorimetry system
acfm	actual cubic feet per minute
ACS	American Chemical Society
Ag	silver
Al	aluminum
API	American Petroleum Institute
As	arsenic
ASME	American Society of Mechanical Engineers
Ba	barium
Br	bromine
Btu/scf	British thermal units per standard cubic foot
Ca	calcium
Cd	cadmium
CEMS	continuous emissions monitoring system
C_x	compound containing 'x' carbon atoms
Cl^-	chloride ion
Cl	chlorine
Co	cobalt
CO	carbon monoxide
CO_2	carbon dioxide
CPM	condensable particulate matter
Cr	chromium
Cu	copper
DI	distilled deionized
DRI	Desert Research Institute
dscfm	dry standard cubic feet per minute
dscmm	dry standard cubic meters per minute
ED-XRF	energy dispersive x-ray fluorescence
EER	GE Energy and Environmental Research Corporation
EC	elemental carbon
EI	electron impact
EPA	Environmental Protection Agency
ERA	Environmental Research Associates
$^{\circ}\text{F}$	degrees Fahrenheit
Fe	iron
FID	flame ionization detection
FPM	filterable particulate matter
FTIR	Fourier transform infrared detection
ft/sec	feet per second
Ga	gallium
GC	gas chromatography
GC/IRD/MSD	gas chromatography/infrared detector/mass selective detector
GC/MS	gas chromatography/mass spectrometry

GE	General Electric
GE EER	General Electric Energy and Environmental Research Corporation
gr/100dscf	grains per hundred standard cubic feet
G-S	Greenburg-Smith
Hg	mercury
H ₂ S	hydrogen sulfide
HCl	hydrochloric acid
HEPA	high efficiency particulate air
HHV	higher heating value
IC	ion chromatography
In	indium
K	potassium
KHP	potassium hydrogen phthalate
La	lanthanum
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
m/sec	meters per second
Mg	magnesium
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
MID	multiple ion detection
Mlb/hr	thousand pounds per hour
MMBtu/hr	million British thermal units per hour
Mn	manganese
Mo	molybdenum
MSD	mass spectrometric detector
MSD/FTIR	mass selective detector/Fourier transform infrared detection
Na	sodium
Na ₂ CO ₃	sodium carbonate
NaCl	sodium chloride
NaHCO ₃	sodium bicarbonate
NaNO ₃	sodium nitrate
NaOH	sodium hydroxide
(Na) ₂ SO ₄	sodium sulfate
NDIR	non-dispersive infrared
NH ₄ ⁺	ammonium ion
(NH ₄) ₂ SO ₄	ammonium sulfate
Ni	nickel
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO ₂	nitrogen dioxide
NO ₃ ⁻	nitrate ion
NO _x	oxides of nitrogen
O ₂	molecular oxygen
OC	organic carbon
P	phosphorus

PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCA	Portland Cement Association
Pd	palladium
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppmv	parts per million (volume)
psig	pounds per square inch (gauge)
PUF	polyurethane foam
QA	quality assurance
Rb	rubidium
RSD	relative standard deviation
S	sulfur
Sb	antimony
Si	silicon
Sn	tin
SO ₂	sulfur dioxide
SO ₄ ⁼	sulfate ion
Sr	strontium
SRM	standard reference material
SVOC	semivolatile organic compound
TFE	tetrafluoroethylene
Ti	titanium
TIGF	Teflon-impregnated glass fiber
Tl	thallium
TMF	Teflon-membrane filter
TOR	thermal/optical reflectance
U	uranium
V	vanadium
VOC	volatile organic compound
XRF	x-ray fluorescence
XAD-4	Amberlite® sorbent resin (trademark)
Y	yttrium
Zn	zinc
Zr	zirconium